CARL TH. PEDERSEN

Some Physico-Chemical Aspects of the Chemistry of Aromatic 1,2-Dithiole Derivatives

ODENSE 1976

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Denne afhandling er i forbindelse med de 16 nedennævnte tidligere offentliggjorte afhandlinger antaget af det naturvidenskabelige fakultetsråd ved Odense Universitet til offentligt at forsvares for den filosofiske doktorgrad.

Odense Universitet, den 7. april 1976

E. Krogh Andersen
h.a.dec.

I C. Th. Pedersen og J. Møller:
Mass Spectra of Phenyl- and Methylsubstituted 1,2-Dithiol-3-ones and 1,2-Dithiol-3-thiones.
Acta Chem. Scand. 26 (1972) 250-256. Ref. 62b

II C. Th. Pedersen, N. L. Huaman og J. Møller:
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Acta Chem. Scand. 26 (1972) 565-572. Ref. 60

III C. Th. Pedersen, N. L. Huaman, R. Pinel og J. Møller:
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Acta Chem. Scand. 26 (1972) 1305-1318. Ref. 123

IV C. Th. Pedersen of V. D. Parker:
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V C. Th. Pedersen, O. Hammerich og V. D. Parker:
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J. Electroanal. Chem. 1972 479-481. Ref. 56

VI C. Th. Pedersen, M. Stavaux og J. Møller:
Mass Spectrometric Fragmentation of 2,6-Bis-(1,2-Dithiole-3-ylidene)cyclohexanethiones and Other Multisulfur Heterocycles Related to the 1,2-Dithiole System.
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J. Am. Chem. Soc. 95 (1973) 4373-4378. Ref. 19

VIII C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, K. Bechgaard, V. D. Parker og C. Th. Pedersen:
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J. C. S. Perkin I (1973) 2837-39. Ref. 119

X C. Th. Pedersen:
Formation of α-(5-Phenyl-1,3-dithiol-2-ylidene)-propanethione from Thioacetic acid and Phenylacetylene.
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XI C. Th. Pedersen og J. Møller:
Thermolysis of 1,2-Dithiolylium Salts in the Ion Source of the Mass Spectrometer.
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XII C. Th. Pedersen og K. Schaumburg:
The Structure of 1,6,6aλ^4-Trithiapentalene and substituted 1,6,6aλ^4-Trithiapentalenes Studied by means of NMR Spectroscopy.
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XIV C. Th. Pedersen, C. Lohse og M. Stavaux:
Photochemistry of Sulphur Compounds Related to the 1,2-Dithiole Series IV.
Photoisomerisation of α-[7-(5-aryl or alkyl-1,2-dithiol-3-ylidene)-4,5,6,7-tetrahydro-1,2-benzodithiol-3-ylidene]ketones.
J. C. S. Perkin I (1974) 2722-24. Ref. 149

XV C. Th. Pedersen, H. Davy, J. Møller og J. Vialle:
Mass Spectrometric Studies of α-(1,3-dithiol-2-ylidene)thio-ketones and thio-aldehydes.
Acta Chem. Scand. Ser. B 28 (1974) 964-65. Ref. 66

XVI C. Th. Pedersen og C. Lohse :
Photochemistry of Sulphur Compounds Related to the 1,2-Dithiole System V.
Formation of 1,2-Dithiolyl Radicals and Dithioketonate Anions in the Photolysis of 3,5-Disubstituted 1,2-Dithiolylium Salts.
Acta Chem. Scand. Ser. B 29 (1975) 831-34. Ref. 25

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Introduction.

Since the structure originally proposed by Arndt[45] for the reaction product of 2,4,6-heptanetrione with phosphorus pentasulfide was questioned in the middle of the fifties[47,48,49], one of the central problems in 1,2-dithiole chemistry has been the structure of 1,6,6aλ^4-trithiapentalenes. Two principal questions which have to be answered are:

1. Is the trithiapentalene nucleus a bicyclic system to which several resonance structures contribute to, or has it to be considered a monocyclic system (a dithiolylidene thione) in such a way that the resulting system consists of two or more valence tautomers which are interconverting very fast?
2. Is the system an aromatic system e.g. a 10π electron system like naphthalene?

During the fifties and sixties the discussion of these structural problems was mainly based on chemical evidence and X-ray data together with some ^{1}H NMR spectroscopic studies.

When we took up these studies in the beginning of the seventies, it was our intention to see if it was possible, by using other physico-chemical methods, to come to a more clear understanding of the physico-chemical and chemical problems in this class of compounds.

It was thought that mass spectrometry could be of some help in solving some of these problems. As mass spectrometric studies on systems with 1,2-dithiole structure had not been published hitherto, it was found necessary to study the fundamental fragmentation of the 1,2-dithiole system upon electron impact, the mass spectra of a series of phenyl and methyl substituted 1,2-dithiole-3-thiones and 1,2-dithiole-ones therefore were recorded (I). The fragmentation observed in these compounds gave a background for the understanding of the fragmentation observed in the more complicated compounds studied (II, III, VI).

The mass spectra of 1,6,6aλ^4-trithiapentalenes (II) exhibited intense molecular ion peaks, which in most cases

were the base peaks in the spectra. This reflects the aromatic character of the system. The general fragmentation was elucidated but no conclusion concerning the problem whether the compounds are monocyclic or bicyclic was obtained, this would also be rather unlikely with a method which investigates such highly excited species.

A class of compounds which often has been named isotrithiapentalenes behaved massspectrometrically in a quite different way, in this case the intensity of the molecular ion peak was smaller and this peak was not the base peak. Based on this we assigned a monocyclic structure to these compounds (a 1,3-dithiol-2-ylidene thione structure) (XV).

The aromatic character of a series of polysulfur compounds related to the 1,2-dithiole system was reflected in their mass spectra as they all show intense molecular ion peaks in the mass spectrometer (VI).

Further, the mass spectra of 1,2-dithiolylidene ketones were studied (III) to see if it was possible in this way to give a contribution to the problem concerning sulfur-oxygen interaction in these compounds. However, we were not able from the study to come to any conclusion concerning this problem.

In the discussion of the bonding of 1,6,6aλ^4-trithiapentalene, a compound where the interaction between the dithiole sulfur atoms and the third sulfur was broken could be of interest. A paper concerning such a key-compound has been published by Behringer[58] who claims to have prepared a trans trithiapentalene. However, we were able to show that this compound was an isotrithiapentalene. The structure elucidation was based on mass spectrometry and chemical evidence (X).

The analogous trans dithiolylidene ketones, however, have been shown to have a transient existence as the isomerization products of 1,2-dithiolylidene ketones upon irradiation with light. (IX) An O-S bonded structure earlier proposed for these photo products[117] could be excluded. The same type of isomerization was observed in higher sulfur analogues of 1,2-dithiolylidene ketones (XIV).

ESR studies of anion radicals derived from substituted trithiapentalenes had shown[54] that the trithiapentalenes had

a mirror plane through C(3a)-S(6a) indicating that the systems were symmetrical. In order to study the ESR spectra of cation radicals of trithiapentalenes the cathodic oxidation of trithiapentalenes was studied (V). The oxidation did not give rise to stable radicals, but to dimeric dications.

As the electrochemical behaviour of 1,2-dithiole derivatives was practically unknown, it was found of interest to see whether such electrochemical dimerization processes were general in the series of 1,2-dithiole compounds or whether it was something characteristic of the trithiapentale system. Cathodic reduction of 3,4-diaryl substituted 1,2-dithiolylium salts gave rise to stable C-C linked dimers (IV), whereas the reduction of the corresponding 3,5-diaryl substituted dithiolylium salts gave stable 1,2-dithiolyl radicals, which could be studied by means of ESR spectroscopy (VII). The radicals dimerized reversibly at a lower temperature and gave C-C linked dimers. The radicals could be reduced further to give anions which isomerized to dithioketonate anions.

The formation of dithiolyl radicals and dithioketonate anions by electrochemical reduction was found in agreement with a CNDO/2 calculation of the stability of these two species (VIII).

It is well established that radicals can be formed photolytically, therefore 3,5 disubstituted 1,2-dithiolylium salts were studied by means of flash photolysis technique and the formation of dithiolyl radicals as well as dithioketonate anions was observed in ethanolic solution. Correspondence was found between the decay rates of the 1,2-dithiolyl radicals in ethanol and the dimerization constants of the electrochemically formed dithiolyl radicals in acetonitrile (XVI).

Dithiolyl radicals were found as a thermolysis product in the thermolytical disproportionation of 1,2-dithiolylium salts in the ion source of the mass spectrometer (XI). It was observed that the molecular ion peak in the mass spectrum corresponded to the radical in cases where stable dithiolyl radicals were generated electrochemically and photochemically. In other cases the molecular ions were derived from thermolysis products with lower molecular weight. In the case of

3-mercaptoalkyl substituted dithiolylium salts no ions corresponding to the formation of radicals were observed (XIII), but fragmentation which was in principle analogous to what was observed for simple dithiolylium salts was found.

Thermolysis in the ion source of the mass spectrometer has thus been found to be a valuable alternative to flash vacuum thermolysis in the study of reactive thermolysis products in cases where the starting materials are not volatile.

It has thus been shown by these studies that a narrow link exists between the electrochemical, photochemical and thermolytical behaviour of 1,2-dithiolylium salts.

^{13}C NMR study of 1,6,6aλ^4-trithiapentalenes (XII) on the basis of the chemical shifts of the carbon atoms and a correlation between calculated charges on carbon atoms and the corresponding ^{13}C chemical shifts shows that the trithiapentalene has to be considered a bicyclic naphthalenelike system. It was observed that the relaxation times of C(2) and C(3) were much alike, which would not be expected for a monocyclic system.

The results obtained in these studies have given new information in areas of the chemistry of 1,2-dithiole compounds which had only been sparingly studied before, i.e. mass spectrometry, electrochemistry and photochemistry. Further, the studies have given new information concerning the structure of trithiapentalenes and point towards a bicyclic aromatic representation for this class of compounds.

To give a more complete description of the problems involved in aromatic 1,2-dithiole chemistry, areas which are outside our own studies have been included, i.e. ESCA and photoelectron spectroscopy, theoretical and X-ray studies. In this way the monograph gives a comprehensive treatment of physico-chemical studies in 1,2-dithiole chemistry in the period 1970-1975.

I. General Introduction.

The term aromatic is a rather diffuse description which has been defined in modern theoretical treatments in many different ways. In this review the term aromatic is not used in any sophisticated way, we will as aromatic systems consider systems which have some benzenoid character and which obey the Hückel 4n+2 rule.

The classes of compounds which will be treated here are: 1,2-dithiolylium salts, trithiapentalenes, extended structures derived from these two classes of compounds, 1,2--dithiol-3-ylidene ketones and aldehydes and analogous to the trithiapentalenes with other heteroatoms in the ring system.

As many reviews concerning these classes of compounds have appeared during the sixties[1-6] we will mainly concentrate

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[1] N. Lozac'h and J. Vialle in N. Kharasch ed. The Chemistry of Organic Sulfur Compounds Vol. 2 p. 257, Pergamon Press 1966

[2] H. Prinzbach and E. Futterer, Adv. Heterocyclic Chem. 7, 39 (1966)

[3] N. Lozac'h in M. J. Janssen ed. Organosulfur Chemistry, Reviews of Current Research p. 179, Interscience Publishers, New York 1967.

on literature from the last five years in this paper. Only physico-chemical aspects will be dealt with. New aspects in synthesis and reactions can be found in[7-9]

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[4] E. Campaigne and R. D. Hamilton, Quart. Reports Sulfur Chem. 5, 275 (1970).

[5] N. Lozac'h, Adv. Heterocyclic Chem. 13, 161, (1971).

[6] E. Klingsberg, Quart. Rev. 23, 537 (1969).

[7] Specialist Periodical Reports, Organic Compounds of Sulphur, Selenium and Tellurium Vol. 1 (1970).

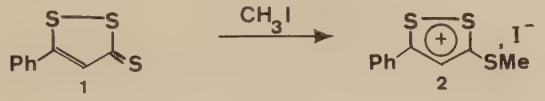
[8] Specialist Periodical Reports, Organic Compounds of Sulphur, Selenium and Tellurium Vol. 2 (1973).

[9] Specialist Periodical Reports, Organic Compounds of Sulphur, Selenium and Tellurium Vol. 3 (1975).

II. 1,2-Dithiolylium Salts.

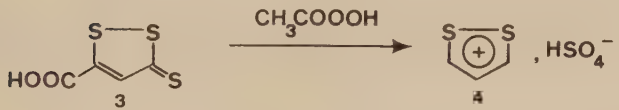
1. Introduction.

The first 1,2-dithiolylium salt 2 was prepared by Böttcher and Lüttringhaus in 1947[10] from the corresponding 1,2-dithiole-3-thione 1.



1 2

The parent compound 4 was prepared by Klingsberg in

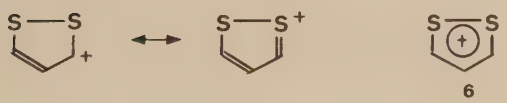


3 4

1960[11] by oxidation of 3 with peracetic acid under spontaneous decarboxylation.

The 1,2-dithiolylium system is formally analogous to the tropylium ion system 5. Each of the two ring sulfur atoms can contribute with its free pair of 3p electrons to give an aromatic 6π electron system 6. cf. p. 16.

5



6

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[10] B. Böttcher and A. Lüttringhaus, Ann. 557, 89 (1947).

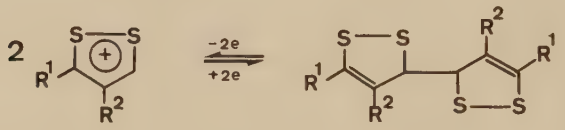
[11] E. Klingsberg, Chem. and Ind, (London). 1568 (1960).

The ion has been given the following names in the literature: dithiolium, dithiylium, dithiolyl and dithiolylium. The last name, which will be used in this review, is in accordance with the IUPAC rule C-83,1[12] as the ion is formally formed by loss of an electron from the free valence position in the corresponding 1,2-dithiolyl radical 7.

7

2. Electrochemistry.

Cathodic reduction of 1,2-dithiolylium salts 8 in dry acetonitrile on a platinum electrode results in the formation of dimers 9[13] probably via a short-lived radical. The structure of the dimer was proved by Raney-nickel desulfurization[14]



8 9

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[12] IUPAC Nomenclature of Organic Chemistry, Section C, Butterworth, London 1965.

[13] C. Th. Pedersen and V. D. Parker, Tetrahedron Letters 767 (1972).

[14] C. Th. Pedersen, Angew. Chem. Int. Ed. 13, 349 (1974).

of 10 which resulted in the formation of 1,2,5,6-tetraphenyl hexane

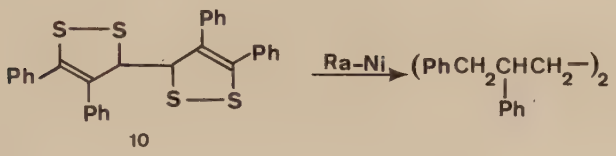

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Fig. 1 shows a typical cyclic voltammogram for a 3,4-diaryl substituted 1,2-dithiolylium salt and its dimer.

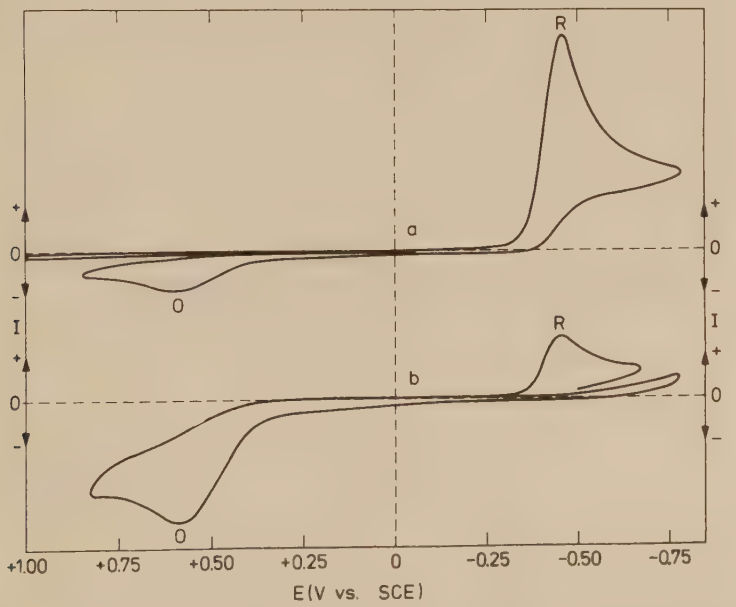


Fig. 1 Cyclic voltammograms of (a) reduction of 8 ($R^1=R^2=Ph$) and (b) oxidation of 9 ($R^1=R^2=Ph$) in acetonitrile[13]. Voltage Sweep rate = 150 mV per second

The electrochemical data for a series of arylsubstituted 1,2-dithiolylium salts are given in Table 1.

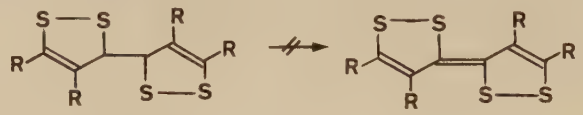
Table 1.

Peak Potentials for the Electrochemical Interconversion:
2 Dithiolylium Ion + 2e $\rightleftarrows$ Bis (1,2-dithiole-3-yl)[13]

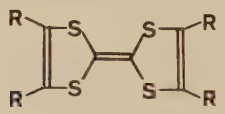
		8	9
R_1	R_2	E_R^a	E_O^b
Ph	Ph	-0.46	+0.59
Ph^c	H	-0.45	+0.70
An^c	H	-0.46	+0.72
An^c	An^c	-0.33	+0.70

a. Peak potential for reduction of 8, b. Peak potential for oxidation of 9, c. p-Anisyl group.

It was found impossible to convert the dimer 10 to the corresponding tetrathiafulvalene 11[14]. This is different from what is observed for the corresponding 1,3-dithiole deri-



10 11



12

vative where the tetrathiafulvalene 12 is easily formed[15,16,17].

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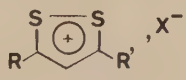
15 D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett and N. D. Canfield, J. Amer. Chem. Soc. 93 2258 (1971).

16 K. M. Pazdro and W. Polackzkowa, Rocz. Chem. 45 811 (1971).

17 L. R. Melby, H. D. Hatzler and W. A. Sheppard, J. Org. Chem. 39 2456 (1974).

Cyclic voltammograms of 1,2-dithiolylium salts of



13

type 13 where R and R' are aryl groups or tert-butyl are quite different from the one shown in Fig. 1[18,19]. The voltammogram of 3,5-diphenyl-1,2-dithiolylium perchlorate is shown in Fig. 2

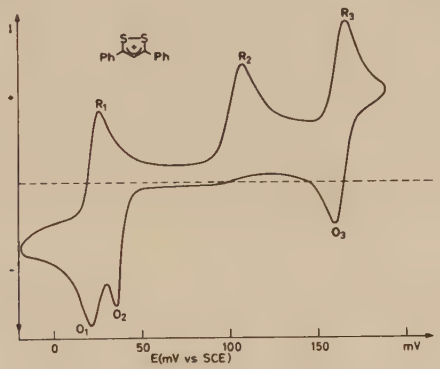


Fig. 2 Steady-state cyclic voltammogram of 14 in CH_3CN containing Bu_4NBF_4(0.2M), sweep rate=300 mV/sec. The initial scan shows all the peaks present in the steady-state voltammogram (ref. 19)

The first couple R^1-O^1 aproaches electrochemical reversibility on a platinium electrode and corresponds to the process 14 ⇄ 15.

14 15

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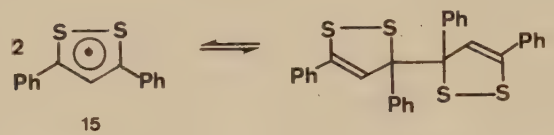
18 C. Th. Pedersen, K. Bechgaard and V. D. Parker, Chem. Comm. 430 (1972)

19 K. Bechgaard, V. D. Parker and C. Th. Pedersen, J. Amer. Chem. Soc. 95 4373 (1973)

The existence and stability of such radicals as 15 has been confirmed by theoretical studies[20,21]. By exhaustive coulometric reduction precisely 1,0 Faraday pr. mole was consumed resulting in a grass green solution with λ_{max}= 400 nm and 650nm. By exclusion of water and oxygen a solution of the radical could be stored for months. On cooling the colour faded due to the dimerization to 16



The following temperature dependence of the equilibrium constant was obtained. Table 2

Table 2

Temperature Dependence of the Equilibrium Constant, $K^{a,b}$ 19.

$$\underset{\text{dimer}}{\underline{\underline{16}}} \overset{K}{\rightleftharpoons} 2 \underset{\text{monomer}}{\underline{\underline{15}}}$$

Temp, °C	+25	+20	+15	+10	+5	0	-5
K(M) × 10^5	57	37	25	16	9.7	5.7	3.2

[a] Total concentration 2(15)+(16) was 1.0×10^{-3}M.

[b] Measured in dichloromethane containing n-Bu_4NBF_4(0.2M)

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20 R. Zahradnik, P Cársky, S. Hunig, G. Kresslich and D. Scheutzow, Int. J. Sulfur Chem., Part C, 109 (1971).

21 C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, K. Bechgaard, V. D. Parker and C. Th. Pedersen, Tetrahedron, 29 3695 (1973)

The radical/dimer equilibrium was found to be dependent on the substituents R and R' as seen from Table 3.

Table 3.

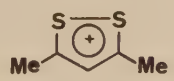
Estimate of Relative Equilibrium Constants for Dimer Dissociation in Dichloromethane at Room Temperature[19]

Compd 13	(Monomer)[a] $\times 10^{-3}$ M	(Dimer)[a] $\times 10^{-3}$ M	K_x/K_3[b]
(p-An, p-An)	o.38	0.43	0.06
(p-An, Ph)	0.51	0.37	0.13
(p-An, p-DMAPh)	0.65	0.30	0.26
(p-Tol, p-Tol)	0.80	0.22	0.54
(p-Tol, Ph)	0.81	0.22	0.55
(Ph, Ph)	0.93	0.16	1.0
(p-BrPh, Ph)	0.94	0.15	1.1

[a] Estimated from peak currents during sweep voltammetry at 150 mV/sec. Substrate concentration = 1.25×10^{-3} M.

[b] Equilibrium constant for the compound divided by K for the reaction $\underline{\underline{15}} \rightleftharpoons \underline{\underline{16}}$.

Bulky substituents must be present in the 3 and 5 positions as shown by the observation that $\underline{\underline{17}}$ gives irreversible electrochemistry of the same type as $\underline{8}$, indicating that the corresponding radical is only short-lived.



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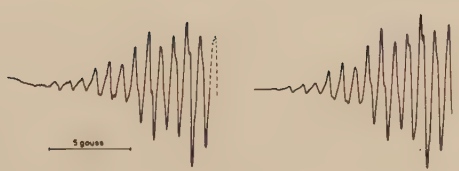
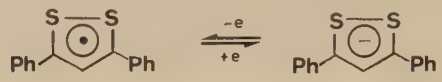


Fig. 3 Experimental (left) and simulated esr spectra of $\underline{\underline{15}}$ (ref. 19)

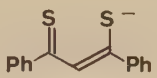
The isotropic g value of 15 was found to be 2.003, very close to the spin-only value of 2.0023.

The second couple R^2-O^2 in Fig 2 which is completely irreversible corresponds to the process 15 $\rightleftarrows$ 18



15 18

The irreversibility is probably due to the chemical transformation of 18 into the dithioketonate anion 19.



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The visible spectra of 15 and 19 are shown in Fig. 4.

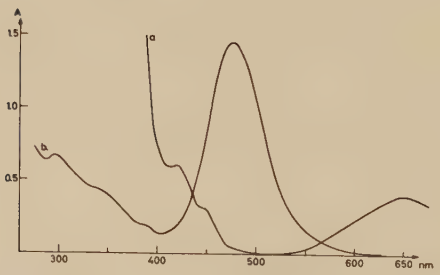
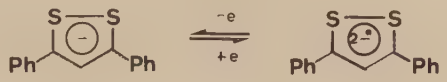


Fig. 4 (a) Visible spectrum of 15 + dimer (total concentration 3.3×10^{-4} M) in CH_3CN containing Bu_4NBF_4(0.1 M). (b) Uv and visible spectrum of 19 (total concentration 5.6×10^{-5} M) in CH_3CN containing Bu_4NBF_4(o.1 M) (ref. 19)

Further reduction resulted in the reversible couple R^3-O^3 which corresponds to the process 18 ⇄ 20

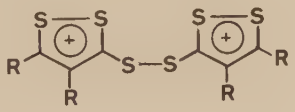


18 20

However, the dianion radical 20 was only stable during the timescale of cyclic voltammetry, it was not possible to prepare it by exhaustive reduction.

Fabian et al[22] have studied the polarography of a series of alkylsubstituted 1,2-dithiolylium salts and have found a linear relationship between the polarographic half wave potentials and the energy of the lowest non occupied orbital.

Bis-dithiolylium ions such as 21 have been reported from the anodic oxidation of 1,2-dithiol-3-thiones[23]



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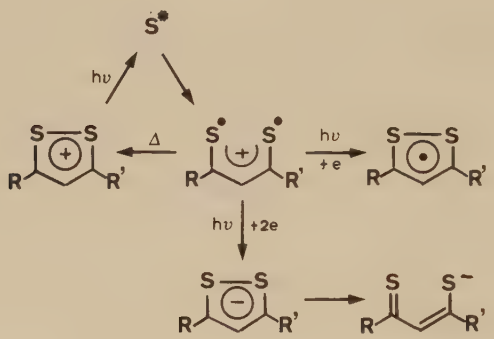
[22] K. Fabian, H. Hartmann, J. Fabian and R. Mayer, Tetrahedron 27, 4705 (1971)

[23] C. Th. Pedersen and V. D. Parker, Tetrahedron Letters, 771 (1972)

3. Photochemistry.

The photochemistry of 1,2-dithiolylium salts has been studied by Pedersen and Lohse[24,25] who have shown that the irradiation of dithiolylium salts in ethanol gives rise to formation of dithiolyl radicals and dithioketonate anions as found for the electrochemical reduction of the same salts.[18,19]

They have proposed the following mechanism for the reaction



In Table 3 are given the rate constants for the 1st order decay of 1,2-dithiolyl radicals in absolute ethanol.

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[24] C. Th. Pedersen and C. Lohse, Tetrahedron Letters, 5213 (1972)

[25] C. Th. Pedersen and C. Lohse, Acta Chem. Scand. B29, 831 (1975).

Table 3.

Rate constants for the 1st Order Decay of 1,2-Dithiolyl Radicals. (ref.25)

R	R^1	k (sec^{-1})
Ph	Ph	903
Ph	An	2020
Ph	4-$CH_3C_6H_4$	895
Ph	4-Br C_6H_4	735
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	880
An	An	2300
tert-Bu	tert-Bu	252
Ph	CH_3	2040
Ph	SCH_3	2480
CH_3	CH_3	4270
H	H	754

The general trend in the lifetimes are the same as found electrochemical for the dimerization of dithiolyl radicals[19] although the radicals here decay by reaction with the ethanol.

The unsubstituted radical is surprisingly stable, there has been given no explanation for this, but the same was observed by thermolytic studies of 1,2-dithiolylium salts in the ion source of the mass spectrometer[26].

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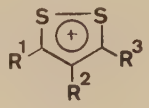
[26] C. Th. Pedersen and J. Møller, Tetrahedron 30, 553 (1974)

4. Mass Spectrometry.

Although 1,2-dithiolylium salts 22 are true salts, and as such not volatile, reproducible mass spectra are obtained on introduction in the ion source of the mass spectro-



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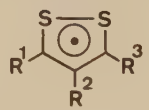
meter[26]. The mass spectra obtained corresponds to thermolysis products which can be rationalized if it is supposed that the primary thermolysis products are radicals or carbenes which give rise to the mass spectra either per se or via secondary transformation products.

If R^1 and R^3 are different from hydrogen the primary products are radicals 23 which, when R^1 and R^2 are phenyl, tert-

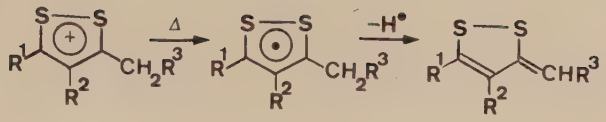


23

butyl or hydrogen, give rise to the molecular peaks in the spectra.

If one of the substituents has a hydrogen in the α-position the radical stabilizes by loss of a proton under formation of 24.

In the case where one of the substituents R^1 and R^3 is hydrogen the primary process is formation of a carbene



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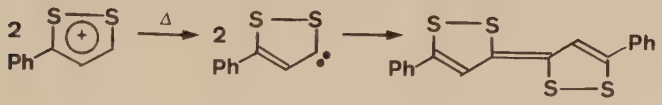
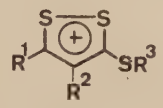
25 which dimerizes with formation of the tetrathiafulvalene 26.



25 26

The pyrolytic behaviour of the 1,2-dithiolylium salts is analogous to that reported for the iso π-electronic pyrylium and thiapyrylium salts[27].

3-Alkyl or aryl-mercapto-1,2-dithiolylium salts 27 have also been subject to thermolytic studies in the mass spectrometer[28].



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[27] G. Hvistendahl, P. Györösi, and K. Undheim, Org. Mass. Spectrometry, 9, 80 (1974)

[28] C. Th. Pedersen, N. L. Huaman and J. Møller, Acta Chem. Scand. B28 1185 (1974).

These salts have been found to behave in most respects like the simple 1,2-dithiolylium salts.

There seems to exist an analogy between the electrochemical, photochemical and thermolytical behaviour of 1,2-dithiolylium salts as radicals are the primary formed products in all three kinds of fragmentation.

5. ESCA and photoelectron spectroscopy:

The S2p binding energies obtained from 1,2-dithiolylium salts are situated halfway between that of 1,2-dithiolane and sulfonium sulfur[29]. This indicates that the normal charge of a sulfonium sulfur atom is shared between 2 sulfur atoms in accordance with the two canonical structures 28 and 29

28 29 6

Schneller and Swartz[30] have studied the binding energies of both the S2p electrons and the C1s electrons in a series of 1,2-dithiolylium salts and conclude from their studies that the dithiolylium salts are best presented by the fully delocalized structure 6.

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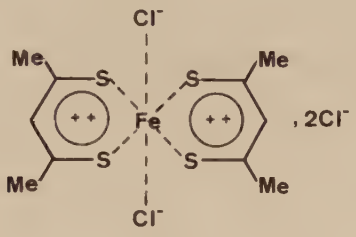
[29] B. J. Lindberg, S. Högberg, G. Malmsten, J. E. Bergmark, Ö Nilsson, S.-E. Karlsson, A. Fahlman, U. Gelius, R. Pinel, M. Stavaux, Y. Mollier and N. Lozac'h, Chemica Scripta, 1, 183, (1971)

[30] S. W. Schneller and W. E. Swartz Jr., J. Heterocyclic Chem. 11, 105 (1974).

6. Structure determinations.

X-ray structure determination of 1,2-dithiolylium salts has been reviewed by Hordvik[31].

A compound obtained by introducing hydrogen sulfide in acetylacetone containing ferric chloride was originally ascribed to the structure 30[32].



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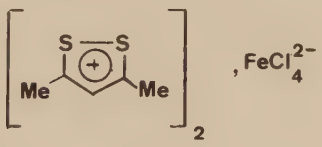
Later it was shown by electronic, infrared, Mössbauer spectra[33] and X-ray structure determination[34,35] that the structure was actually 31.



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31 A. Hordvik, Quart. Reports Sulfur Chem. 5, 21 (1970).

32 K. Knauer, P. Hemmerrich and J. D. W. van Voorst, Angew. Chem. int. Edn. 6, 262 (1967).

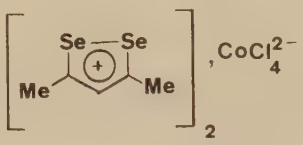
33 G. A. Heath, R. L. Martin and I. M. Stewart, Austral. J. Chem. 22, 83 (1969).

34 H. C. Freeman, G. H. W. Milburn, C. E. Nockolds, R. Mason, G. B. Robertson and G. A. Rusholme, Acta Cryst. B30 886 (1974).

35 H. C. Freeman, G. H. W. Milburn, C. E. Nockolds, P. Hemmerrich and K. H. Knauer, Chem. Comm. 55 (1969).

Compounds with other metals such as Mn,Fe, Co,Ni and Cu have been prepared[33] and so have salts with the 3,5-diphenyl-1,2-dithiolylium ions[36].

Heath et al[33] have prepared analogous 1,2-diselenolylium salts e.g. 32 for structural comparison.



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7. Theoretical Studies.

Palmer and Findlay have in a study of a series of sulfur heterocycles[37] studied 1,2-dithiolylium salts using a linear combination of gausian orbitals (LCGO) with 10 s and 6 p orbitals for sulfur which were augmented with a single gausian for each of the five 3d orbitals where appropriate. Their conclusion from the calculation which include thiophene, 1,2- and 1,3-dithiolylium salts, thiapyrylium salts and 1,6,6aλ^4-trithiapentalenes, is that the d orbitals only play a minor role.

Pfister et al[38] have studied the electronic spectra of unsubstituted, 3- and 4-methyl, 3- and 4-phenyl-1,2-dithiolylium salts and compared the experimental spectra with

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36 R. Mason, G. B. Robertson and G. A. Rusholme, Acta Cryst. B30, 894 (1974).

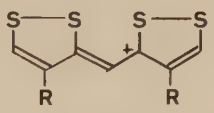
37 M. H. Palmer and R. H. Findlay, Tetrahedron Letters, 4165 (1972)

38 C. Guimon, D. Gonbeau and G. Pfister-Guillouzo, Tetrahedron, 29, 3399 (1973).

calculated spectra using CNDO/S methods. They find that they obtain a better agreement when d orbitals are included in the calculations although the d orbitals don't contribute much to the total energy.

Electronic spectra of 1,2-benzodithiolylium salts, 3-mercapto-1,2-benzodithiolylium salts, 1,2-dithiolylium salts and 3-mercapto-1,2-dithiolylium salts have been interpreted by Fabian et al[39] by PPP methods, and results which fit nicely with experimental spectra are obtained.

Among other polymethine dyes in the 1,2- and 1,3-dithiolylium series Fabian et al have studied compounds of type



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33 by PMO and PPP methods and have obtained a nice agreement between calculated and experimental data[40,41].

Pfister et al have been able to explain the modification of the electronic spectrum of 1,2-dithiole-3-thione upon protonation[42] forming the mercaptodithiolylium ion 34 by CNDO/2 methods.

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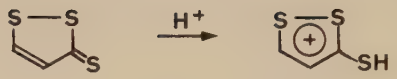
[39] J. Fabian, K. Fabian and H. Hartmann, Theor. Chim. Acta 12, 319 (1968)

[40] J. Fabian and H. Hartmann, Tetrahedron, 29, 2597 (1973).

[41] J. Fabian, H. Hartmann and K. Fabian, Tetrahedron, 29, 2609 (1973).

[42] D. Gonbeau, C. Guimon and G. Pfister-Guillouzo, Tetrahedron, 29, 3599 (1973).



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Further examples on calculation of 1,2-dithiolylium salts are given by Fabian[43,44].

Pfister et al[21] have examined the electrochemical reduction of 1,2-dithiolylium salts by CNDO/2 methods. The experimentally observed formation of dithiolyl radicals 15 and dithioketonate anions 19 is in agreement with the calculations.

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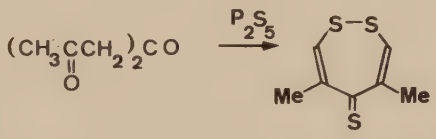
[43] R. Mayer, H. Hartmann, J. Fabian and A. Mehlhorn, Z. Chem. 7, 209 (1967).

[44] J. Fabian, J. prakt. Chem. 315, 690 (1973).

III. 1,6,6aλ^4-Trithiapentalenes.

1. Introduction.

In 1925 Arndt et al[45] reacted 2,4,6-heptanetrione with phosphorus pentasulfide and obtained a compound to which they ascribed the structure 35, which was not



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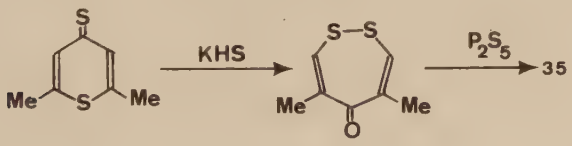
questioned for many years. In 1953 Traverso and Sanesi reacted 4-thiapyran thiones 36 with potassium hydrogen sulfide and isolated a compound which they formulated as 37[46] as it was converted to 35 by reaction with phosphorus pentasulfide.



36 37

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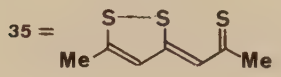
[45] F. Arndt, P. Nachtwey and J. Pusch, Ber. 58, 1633 (1925)

[46] G. Traverso and M. Sanesi, Ann. Chim. (Rome) 43, 795 (1953).

In 1958 a new structure was proposed simultaneously by Guillouzo by means of IR-spectroscopic studies[47] and by Bezzi and Carbuglio[48] on the basis of X-ray studies. The structures proposed were 38 and 39.



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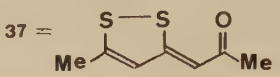

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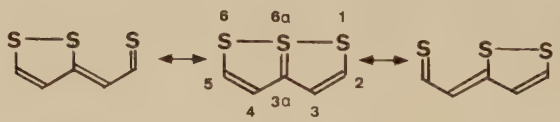
The structure 38, however, was not in accordance with the observation that the two sulfur distances were equal[48] and that the ^{1}H NMR spectrum showed that the methyl groups were identical[49]. These problems were solved by the introduction of the concept of no-bond single-bond resonance as described by the three canonical structures 40, 41 and 42.[49]



40 41 42

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47 G. Guillouzo, Bull. Soc. Chim. Fr. 1316 (1958).

48 S. Bezzi, M. Mammi and C. Carbuglio, Nature, 182, 247 (1958); S. Bezzi, C. Carbuglio, M. Mammi and G. Traverso, Gazz. Chim. Ital. 88, 1226 (1958); M. Mammi, R. Bardi, C. Carbuglio and S. Bezzi, Acta Cryst.13, 1048 (1960)

49 H. G. Hertz, G. Traverso and W. Walter, Ann. 625, 43 (1959)

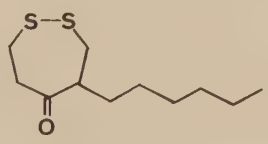
The fact that we have to deal with resonance structures where the same atoms are not bonded in the different structures has given serious problems in finding a correct nomenclature for these compounds.

The following names have been used for the system: meribicyclo-3,5-epidithio-2,4-pentadienethione, thiothophthene, thiathiophthene, [1,2]dithiolo[1,5-b][1,2]dithiole, α-(1,2-dithiol-3-ylidene)thioacetaldehyde, 1,6,6a^{IV}S-trithiapentalene and 1,6,6aλ^4-trithiapentalene.

The last two names are the best as they are in accordance with the IUPAC rules. The symbol ^{IV}S is used in the inorganic chemistry to indicate the oxidation state of the element. It is therefore proposed that λ^4 is used instead, as λ is the number of bonds to an atom[50].

Compounds with structures 35 and 37 have never been prepared and it has been suggested by Zahradnik that for theoretical reasons 35 must be unstable[53].

A compound with the structure 43 has recently been



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isolated from some Hawaiian algae Dictyopteris plagiogramma and D. australis[51,52].

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[50] IUPAC Nomenclature of Organic Chemistry, Section D, IUPAC Information Bulletin 1973.

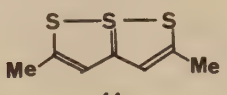
[51] P. Roller, K. Au and R. E. Moore, Chem. Comm. 503 (1971).

[52] R. E. Moore, Chem. Comm. 1168 (1971).

[53] R. Zahradnik, Adv. Heterocyclic Chem. 5, 30 (1965).

2. Electrochemistry.

The electrochemical reduction of the 1,6,6aλ^4-trithiapentalenes 44 - 48 to the corresponding anion radicals has



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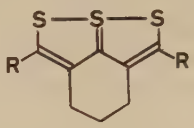
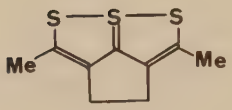


46 R: Me
47 R: Et
48 R: i-Pr



45

been described[54,55]. The chemistry of the anion radicals was not studied, it was only noticed that the stability of the anion radicals increases in the order 44<45<46<47<48. The half-lifetime of $44^{-\bullet}$ is only a few minutes at 20°C, whereas $48^{-\bullet}$ is stable over a period of several hours. The ESR spectra of the anion radicals were studied in the temperature range +25 - -40°C and the radical anions were found to retain a mirror plane passing through C(3a)-S(6a) indicating that the system is symmetrical.

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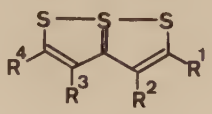
54 F. Gerson, R. Gleiter, J. Heinzer and H. Behringer, Angew. Chem. 82, 294 (1970).

55 F. Gerson, J. Heinzer and M. Stavaux, Helv. Chim. Acta 56, 1845 (1973).

The ESR spectra of $\underline{46}^{-\cdot}$, $\underline{47}^{-\cdot}$ and $\underline{48}^{-\cdot}$ displayed a marked temperature dependence due to inversion of the 3,4-trimethylene chain and the restricted rotation of the 2,5 alkyl groups.[55]

Voltammetric studies of 49 showed that the oxidation was electrochemically irreversible, indicating that no stable



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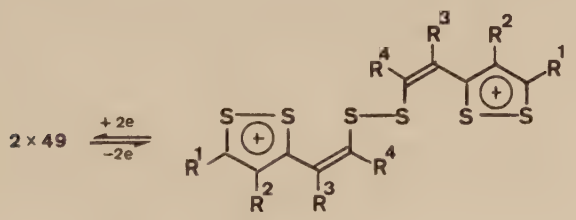
cation radicals were formed[56]. This is consistent with the lack of an ESR signal from the resulting solution. The electrochemistry was consistent with the formation of the dimeric β,β'-dithio-bis(3-styryl-5-phenyl-1,2-dithiolylium) dication 50. ($R^1 = R^4 = Ph$, $R^2 = R^3 = H$)



50

Reduction of the dimers resulted in regeneration of 49. 49 ($R^1 = R^4 = Ph$, $R^2 = R^3 = H$) has λ_{max} 258 and 511nm whereas 50 ($R^1 = R^4 = Ph$, $R^2 = R^3 = H$) showed absorption at 258nm and 494, indicating that the trithiapentalene system is no longer present in the oxidized product.

The voltammetric and coulometric data for a series of substituted 1,6,6aλ^4-trithiapentalenes are shown in Table 4.

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[56] C. Th. Pedersen, O. Hammerich and V. D. Parker, J. Electroanalyt. Chem. 38, 479 (1972).

Table 4.

Voltammetric and Coulometric Data for Oxidation of 49 and Reduction of 50[56].

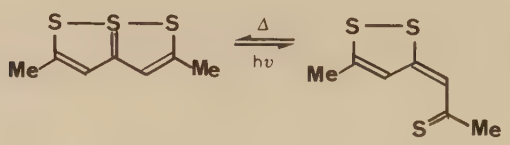
R^1	R^2	R^3	R^4	E_p^O/V	E_p^R/V	n^O	n^R	% Recovery
Ph	H	H	Ph	+0.87	+0.32	1.0	0.8	100
Ph	Ph	H	Ph	+1.16	-0.03	1.0	1.0	87
Ph	H	H	An	+0.73	+0.42	1.0	0.7	84
An	H	H	An	+0.69	+0.30	1.0	0.7	100
An	An	H	An	+0.80	+0.29	1.0	0.8	86
An	An	An	An	+0.84	-0.35	1.0	1.1	97

An=p-Anisyl

Peak potentials refer to the aq.satd. calomel electrode and are for oxidation or reduction at a platinum electrode.

3. Photochemistry.

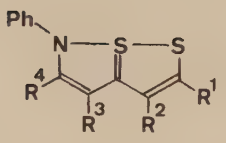
In the same way as 1,2-dithiolylidene ketones are converted to trans isomers upon irradiation (cf. pag. 54), 44 has been reported to be transformed to the trans isomer 51 photochemically[57]. The same was observed for a series of



44 51

6-aza-1,6aλ^4-dithiapentalenes 52.

[57] G. Calzaferri, R, Gleiter, R. Gygax, K.-H. Knauer, E. Schmidt and H. Behringer, Helv. Chim. Acta, 56 2584 (1973).



52

52A : $R^1=R^4=Me$
$R^2=R^3=H$
52B : $R^1=R^4=Ph$
$R^2=H$, $R^3=CN$

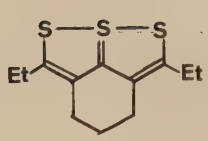
The kinetic data shown in Table 5 were obtained.

Table 5.

Kinetic Data for the Thermal Back Reaction[57].

Compound	Solvent	k_{25}^{o} S^{-1}	τ_{25}^{o} S	E_a kcal/mol	$\Delta G^{\neq}_{25}{}^{o}$ kcal/mol	$\Delta S^{\neq}_{25}{}^{o}$ c.u.
39	Toluene	5.9×10^{-4}	1176	10.1	21.9	-41.5
39	Ethanol	4.7×10^{-3}	148	11.6	20.6	-32.3
44	Ethanol	616.6	1.1×10^{-3}	9.4	13.7	-16.1
44	Acetonitrile	17.0	4.1×10^{-2}	9.7	15.8	-22.5
52A	Toluene	322.1	2.2×10^{-3}	13.6	14.0	- 3.5
52A	Ethanol	204.2	3.4×10^{-3}	10.8	14.3	-13.9
52A	Acetonitrile	550.0	1.3×10^{-3}	11.5	10.9	- 9.5
52B	Ethanol	565.0	1.2×10^{-3}	10.2	13.7	-13,9
52B	Acetonitrile	550.0	1.3×10^{-3}	10.5	9.9	-12.8

That the photoproducts formed are trans isomers are suggested on the fact that the kinetic data and the activation parameters are very much like those of 1,2-dithiolylidene ketones, and from the observations that the compounds 53 and 54 are photostable.



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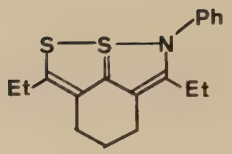
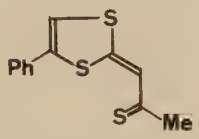


54

It has been claimed that trans 1,6,6aλ^4-trithiapentalenes should be stable compounds[58], but a compound which has been described as a stable trans trithiapentalene has been shown to be a 1,3-dithiolylidene thione 55[59].



55

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[58] H. Behringer, Chimia, 19, 132 (1965).

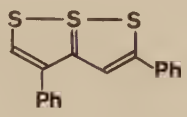
[59] C. Th. Pedersen, Acta Chem. Scand. B28, 367 (1974).

4. Mass spectrometry.

Although mass spectra of trithiapentalenes have been used in many cases as structural proof in connection with new synthesis mechanistic studies are few[60,61].

The general feature of the mass spectra is that the trithiapentalenes behave as aromatic compounds giving rise to intense molecular ions[60].

Other prominent peaks in the spectra are due to the loss of hydrogen and SH from the molecular ions, The M-SH



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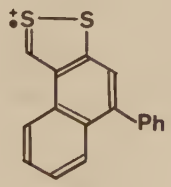
peak derived from 56 has been ascribed to the 1,2-dithiolonaphthalene structure 57, which is analogous to the structure of



57

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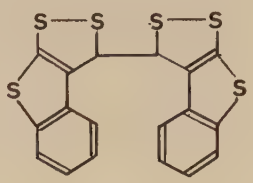
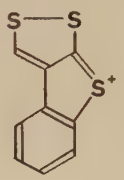
60 C. Th. Pedersen, N. L. Huaman and Jørgen Møller, Acta Chem. Scand. 26, 565 (1972).

61 C. Th. Pedersen, J. Møller, H. Davy and J. Vialle, Acta Chem. Scand. B30 (1976) in press.

the photoproduct 58A obtained from 4-phenyl-1,2-dithiol-3-thione[62a], and the M-H ion 58B derived from 1,2-dithiol-3-thiones[62b] as ring closure to a phenyl substituent occurs in all cases.



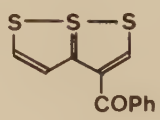
58A



58B

It was observed that if the mass spectrometer was contaminated with sulfur compounds, intense peaks due to the loss of sulfur were present[60]. This is probably due to a catalytic effect.

Surprisingly the substitution pattern in aryl substituted trithiapentalenes had only a small influence on the fragmentation[60]. If the trithiapentalene was substituted with functional groups such as 59 and 60 a greater dependence on



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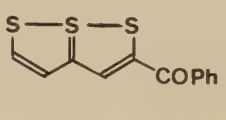

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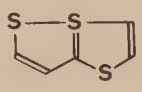
62a P. de Mayo and H. Y. Ng, Tetrahedron Letters, 1561 (1973).

62b C. Th. Pedersen and J. Møller, Acta Chem. Scand. 26, 250 (1972).

the substitution was observed[61]. In 60 the base peak is m/e 159 corresponding to loss of [PhCO + S], this peak is in the spectrum of 59, only 30%. In 59 the base peak is due to m/e 77, which is Ph^+, this peak is only 15% in the spectrum of 60.

The reaction of activated acetylenes with 1,2-dithiole-3-thiones gives rise to compounds which can either be formulated as 1,3aλ^4,4-trithiapentalenes 61 or as 1,3-dithiolylidene thiones 62[63,64,65].



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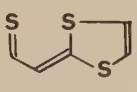

62

Mass spectrometric studies of these compounds, however, show, that they do not behave like an aromatic bicyclic system as 61[59,66]. The principal fragmentation of the compounds is a retro-cycloaddition with loss of acetylenes and reformation of the 1,2-dithiole-3-thione 63.

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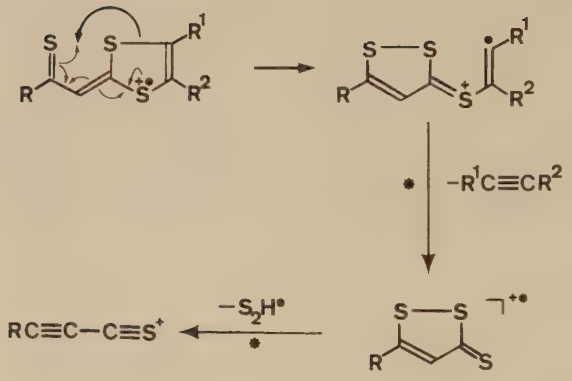
63 H. Davy, M. Demuynck, D. Paquer, A. Rouessac and J. Vialle Bull. Soc. Chim. Fr. 2057 (1968).

64 H. Behringer, D. Bender, J. Falkenberg and R. Wiedenmann Chem. Ber. 101, 1428 (1968).

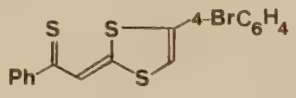
65 D. B. J. Easton and D. Leaver, Chem. Comm. 585 (1965).

66 C. Th. Pedersen, H. Davy, J. Møller and J. Vialle, Acta Chem. Scand, B28, 964 (1974).



63

This is also in accordance with the observation that the distance between the two "disulfide" sulfur atoms in 64 is 2.91 Å, which is longer than found in 1,6,6aλ^4-trithiapentalenes[67]. (cf. Table 6).



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[67] R. J. S. Beer, D. Frew, Johnson P. L. and I. C. Paul, Chem. Comm. 154 (1970).

5. ESCA and photoelectron spectra.

Electron binding energies of the three sulfur atoms in trithiapentalenes should, a priori, be considered as a good indication of symmetry or non symmetry in the trithiapentalene system. If the compounds are symmetrical, two signals with the intensity ratio 2:1 should be found in the ESCA spectrum, whereas an unsymmetrical structure should give rise to three signals with the intensity ratio 1:1:1.

If we have to deal with a system of fast interconverting valence tautomers, it should be possible to see the different tautomers since the X-ray absorption-photoelectron-ejection process occurs in 10^{-14}-10^{-16} sec.

Clark et al[68] have studied the core binding energies of the S2p electrons in a series of trithiapentalenes and have come to the conclusion that unsubstituted and symmetrically substituted trithiapentalenes have a symmetrical structure.

Lindberg et al have reached the opposite conclusion[29]. It has hitherto been a serious problem that the ESCA spectra could not be fully resolved, and broad lines corresponding to the unresolved $S2p_{1/2,3/2}$ complex line pattern were used. Lindberg et al have used the line width of elemental sulfur as a standard for the mathematical deconvolution of the experimental spectra and they can only make a satisfactory deconvolution if they use a 1:1:1 model.

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[68] D. T. Clark and D. Kilcast and D. H. Reid, Chem. Comm. 638 (1971).

Recently Gelius et al[69a,69b] have obtained the gas phase ESCA spectrum of the parent 1,6,6aλ^4-trithiapentalene with a monochromator which is able to resolve the $S2p_{1/2,3/2}$ doublet. They have obtained the spectrum shown in Fig. 6.

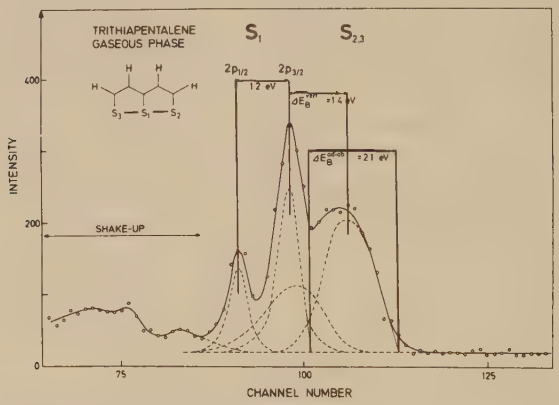

Fig. 6. Spectrum of the S2p lines of trithiapentalene recorded in the gaseous phase[69a].

The broad $S2p_{1/2,3/2}$ line to the right which has twice the area of the two lines to the left is ascribed to the outer sulfur atoms S(1) and S(6) whereas the doublet corresponds to S(6a).

It has not been possible to resolve the signal from the outer sulfur atoms further. The strong broadning of this signal is caused by the loss of symmetry when the photoionization takes place from one of the outer sulfur atoms whereas the symmetry is preserved when the ionization takes place at the central sulfur atom.

69a U. Gelius, E. Basilier, S. Svensson, T. Bergmark and K. Siegbahn, J. Electron. Spectr. 2, 405 (1974).

69b U. Gelius, J. Electron. Spectr. 2, 985 (1974).

The result obtained in this study is thus in agreement with a symmetrical structure.

Coffey has obtained an ESCA spectrum of 2,5-diphenyl-1,6,6aλ^4-trithiapentalene[70,71] which is interpreted in the way that the compound is unsymmetrical, but there is some evidence that this spectrum should be taken with some reservation[72].

Gleiter et al[73] have studied the He-584 Å photoelectron spectra of a series of trithiapentalenes. They find that EH and CNDO/2 calculation of the orbital energies for an unsymmetrical structure gives energies which are very close to the energies obtained from the photoelectron spectra.

Thus it seems impossible at present to come to any definite conclusion about the structure of trithiapentalenes on the basis of photoelectron or ESCA spectroscopy. The most serious problems are probably due to the unusually broad sulfur line.

6. Structure determination.

Since it was shown by X-ray crystallography that the structure originally proposed by Arndt was wrong[45], structure determination by X-ray has been the most used method to obtain new information concerning the trithiapentalene system[74].

In Table 6 the two sulfur distances in a series of trithiapentalenes are shown.

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70 M. D. Coffey, Diss. Purdue University 1972.

71 K. Siegbahn in D. A. Shirley ed. Electron Spectroscopy, North-Holland Publishing Company, Amsterdam 1972.

72 D. T. Clark, Int. J. Sulfur Chem.C. 7, 11 (1972).

73 R. Gleiter, V. Hornung, B. Lindberg, S. Högberg and N. Lozac'h Chem. Phys. Letters, 11, 401 (1971).

74 A. Hordvik and J. Saethre, Israel J. Chem. 10, 239 (1972).

Table 6.

S-S Distances in Trithiapentalenes [49]

R^1	R^2	R^3	R^4	S(1)-S(6a)	S(6a)-S(6)	Ref.
H	H	H	H	2.363	2.363	75,76
Me	H	H	H	2.425	2.301	77
Me	H	H	Me	2.358	2.358	78
Me	H	Ph	H	2.481	2.242	79
Ph	H	H	Ph	2.362	2.304	80,81
Ph	H	Ph	H	2.499	2.218	82
H	Ph	Ph	H	2.232	2.434	83
Ph-NMe_2-4	H	Ph	H	2.348	2.350	84,85
Ph	Me	H	Ph	2.255	2.398	86
SMe	NH_2	H	Ph	2.375	2.266	87
Ph-Br-4	H	PhCO	SMe	2.168 2.163	2.454 2.561	88
Ph	Ph	Ph	H	2.270	2.375	89
Ph	Me	Me	Ph	2.303	2.303	90
Ph	$-CH_2-CH_2-$		Ph	2.351	2.351	91
Ph	$-CH_2-CH_2-CH_2-$		Ph	2.329	2.288	92
Ph	Ph	Ph	Ph	2.312	2.312	93

[75] L. K. Hansen and A. Hordvik, Acta Chem. Scand. 24, 2246 (1970).

[76] L. K. Hansen and A. Hordvik, Acta Chem. Scand. 27, 411 (1973).

[77] A. Hordvik and L. J. Sæthre, Acta Chem. Scand. 26, 1729 (1972).

[78] F. Leung and S. C. Nyburg, Chem. Comm. 137 (1969).

[79] A. Hordvik and K. Julshamn, Acta Chem. Scand. 25, 1835 (1971).

[80] A. Hordvik, Acta Chem. Scand. 22, 2397 (1968).

[81] A. Hordvik, Acta Chem. Scand. 25, 1583 (1971).

[82] A. Hordvik, E. Sletten and J. Sletten, Acta Chem. Scand. 23, 1852 (1969).

[83] P. L. Johnson and I. C. Paul, Chem. Comm. 1014 (1969).

[84] A. Hordvik and L. J. Sæthre, Acta Chem. Scand. 24, 2261 (1970).

[85] A. Hordvik and L. J. Sæthre, Acta Chem. Scand. 26, 3114 (1972).

[86] A. Hordvik, O. Sjølset, L. J. Sæthre, Acta Chem. Scand. 26, 1297 (1972).

[87] A. J. Barnett, R. J. S. Beer, B. V. Karaoghlanian, E. C. Llaguno and I. C. Paul, Chem. Comm. 836 (1972).

[88] S. M. Johnson, M. G. Newton and I. C. Paul, J. Chem. Soc. (B), 986 (1969).

[89] A. Hordvik, Acta Chem. Scand. 25, 1822 (1971).

[90] A. Hordvik, O. Sjølset and L. J. Sæthre, Acta Chem. Scand. 27, 379 (1973).

[91] B. Birknes, A. Hordvik and L. J. Sæthre, Acta Chem. Scand. 27, 382 (1973).

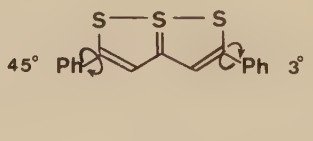
[92] B. Birknes, A. Hordvik and L. J. Sæthre, Acta Chem. Scand. 26, 2141 (1972).

[93] O. Hjellum and A. Hordvik, Acta Chem. Scand. 27, 2666 (1973).

It can be seen from table 6 that the two sulfur distances S(1)-S(6a) and S(6a)-S(6) are normally equal when the system is symmetrically substituted and unequal in unsymmetrically substituted systems.

There has been some discussion whether the fact that the equal sulfur distances found in e.g. 2,5-dimethyl-1,6,6aλ^4--trithiapentalene can be taken as evidence that the system is really symmetrical or whether the equivalence of the two bonds is the result of the solid phase being statistically disordered combination of compounds with a long and a short sulfur distance[94]. This last possibility was ruled out by Leung and Nyburg[78] in a re-examination of the structure. In disordered crystals of such compounds a doubling of the peaks on the electron density distribution should be observed, but such a doubling was not found.

It can be seen from Table 6 that not all symmetrically substituted trithiapentalenes have equal sulfur distances, it is e.g. not the case for 2,5 and 3,4-diphenyl-1,6,6aλ^4-trithiapentalene, This lack of symmetry is caused by a torsion of the phenyl groups in the crystals, the phenyl groups are not situated in the plane of the trithiapentalene part as seen from 65 and 66. The effect of this torsion observed on the sulfur



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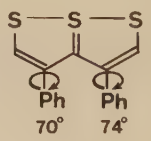

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94 S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer and D. Cartwright, Chem. Comm. 1170 (1967).

distances is consistent with CNDO calculations carried out by Hordvik et al[95].

Hordvik et al have also found that there is agreement between the calculated influence of methyl and phenyl substituents on the S-S bond length and experimental data. A 2-methyl group causes a lengthening of the S(1)-S(6a) bond whereas a 3-methyl group has the opposite effect. A 2-phenyl group has a lengthening effect on the sulfur distance dependent on the twist angle of the phenyl plane. The effect is near zero at an angle of 0° and most pronounced at 90°. A 3-phenyl group shortens the same bond but the effect is only small and independent of the twist angle of the phenyl group.

It is obvious from this discussion that there are great problems in using X-ray data from crystal determination in the discussion of the structure of the isolated trithiapentalene molecule. The anomalies observed may be caused by crystal packing. It is therefore of great importance that a structure determination by electron difractommetry in the gas phase of the unsubstituted trithiapentalene has been made[96]. Calculated radial distribution curves fit nicely with the experimental curves if a symmetrical model is used for the calculation, whereas calculation based on an unsymmetrical model is in poorer agreement with the observed results. These observations indicate that 1,6,6aλ^4-trithiapentalene has C_{2v} symmetry in the gaseous state where there is little interaction between the molecules.

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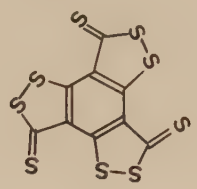
[95] L. K. Hansen, A. Hordvik and L. J. Sæthre, Chem. Comm. 222 (1972).

[96] Q. Shen and K. Hedberg, J. Amer. Chem. Soc. 96, 289 (1974).

A compound prepared by Brown[97] and originally ascribed to the thione structure 67 has by X-ray studies



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been found to be more correctly described as the condensed trithiapentalene 68[98], which is a thiaanalogue of coronene.

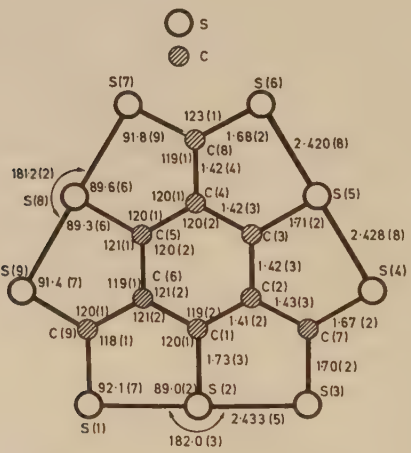

Fig. 7. Bond lengths (Å) and bond angles (°) in S_9C_9 (68)[98]

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97 J. P. Brown and T. B. Gay, J. C. S. Perkin I, 866 (1974).

98 L. K. Hansen and A. Hordvik, Chem. Comm. 800 (1974).

7. Theoretical Studies.

If we try to explain the properties of trithiapentalenes outlined hitherto by classical theories using classical structure with normal σ and π bonds, serious difficulties arise as pointed out by Johnstone and Ward[99].

Johnstone and Ward have used a description for the trithiapentalene which includes the intervention of the 3d orbitals of S(6a) which they consider to be p^2d hybridized. They found that the π-π transitions as well as the ionization potential of trithiapentalene could be predicted from SCF LCAO calculations with PPP approximation on the basis of their hypothesis.

Yamabe et al[100] have calculated the electronic structure and the electronic transitions of the unsubstituted trithiapentalene and 2,5-dimethyl-1,6,6aλ^4-trithiapentalene using the semi empirical ASMO SCF method and have obtained satisfactory agreement between predicted and experimental electronic spectra.

Clark and Kilcast[101] have made a CNDO/2 calculation on the parent trithiapentalene as well as on the 2- and 3-methyl derivatives. Whereas earlier studies have been centered round the electronic structure of the trithiapentalenes Clark and Kilcast have tried to calculate reactivities too. The results obtained by them indicate that the 3 position should be the preferred position for electrophilic substitution, which is in accordance with experimental evidence for e.g. bromina-

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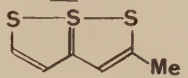
99 R. A. W. Johnstone and S. D. Ward, Theor. Chim. Acta, 14, 420 (1969).

100 H. Yamabe, H. Kato and T. Yonezawa, Bull. Chem. Soc. Japan, 43, 3754 (1970).

101 D. T. Clark and D. Kilcast, Tetrahedron, 27, 4367 (1971).

tion[102] and formylation[103]. Further, some tendency to react on S(1) and S(6) should be present. This is in agreement with the observation that these sulfur atoms can be methylated with methyl iodide[104] or trimethoxonium tetrafluoroborate[105]. The 2 position is predicted as the favoured position for nucleophilic attack. Nucleophilic attack has not been much studied experimentally, but attack by $C_2H_5O^-$ has been described[106].

Clark and Kilcast have also tried to estimate the acidities of the methyl protons in 69 and 70. The calculations show that 69 should be more acidic than 70 in accordance with the observation that 69 condenses readily with benzaldehyde to give the styryl substituted 71[107] whereas 70 does not condense.



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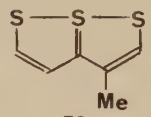

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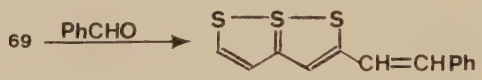

71

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102 R. J. S. Beer, D. Cartwright, R. J. Gait and D. Harris, J. Chem. Soc. (C), 963 (1971).

103 J. Bignebat and H. Quiniou, C. R. Acad. Sci. Paris, 267, C, 180 (1968).

104 E. Klingsberg, J. Org. Chem. 33, 2915 (1968).

105 H. Behringer and J. Falkenberg, Chem. Ber. 102, 1580 (1969).

106 R. J. S. Beer, R. P. Carr, D. Cartwright, D. Harris and R. A. Slater, J. Chem. Soc. (C) 2490 (1968).

107 M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr. 2077 (1968).

Gleiter and Hoffmann[108] have treated the trithiapentalene problem as a special case in an analysis of electron-rich 3-center bonds. They consider the three sulfur atoms a linear system where 3 orbitals are occupied by four electrons for σ-bonding, and π-bonding is superimposed. The stabilization obtained in this way is not expected to be great since the p_π-p_π overlap is still small when the equilibrium distance for a three-center bond involving second-row

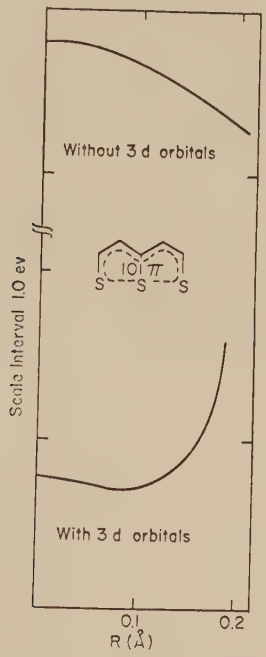

Fig.8 Potential energy curves for horizontal displacement of the central sulfuratom of 1,6,6aλ⁴-trithiapentalene with and without 3d orbitals on S. The horizontal axis measures displacement of the central sulfuratom from the symmetrical position. (ref. 108)

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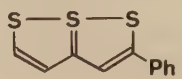
[107] M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr. 2077 (1968).

[108] R. Gleiter and R. Hoffmann, Tetrahedron 24, 5899 (1968).

elements is reached. The potential energy of the S(1)-S(6a)-S(6) system as a function of the displacement of S(6a) from an equilibrium location between S(1) and S(6) shows a very flat minimum corresponding to a symmetrical structure if d orbitals are included in the calculation; if d orbitals are not included an unsymmetrical structure is favoured.

Hansen et al[95] have calculated the energies of a series of trithiapentalenes by using the CNDO/2 method, and they have correlated these energies with X-ray data for the compounds 69, 70, 72 and 73 and have found a close correlatio



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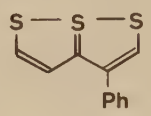

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with the potential curve Fig. 9. Fig. 10 shows the effect of twisting a phenyl substituent.

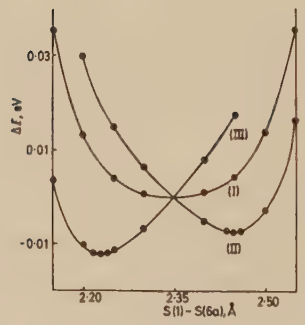


Figure 9 The change ΔE in CNDO/2 total energy for compounds (I)=41, (II)=69 and (III)=70 as a function of the S(1)-S(6a) bond length.

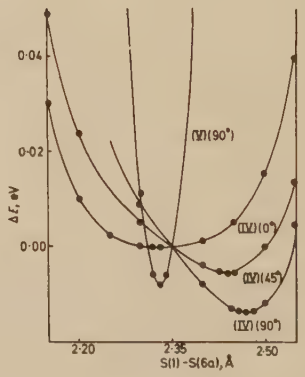
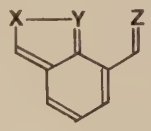


Figure 10 The change ΔE in CNDO/2 total energy for (IV)=72, (V)=73 as a function of the S(1)-S(6a) bond length. The twist angle of the phenyl group is indicated.

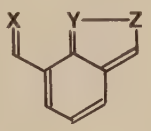
The energy curve for 1,6,6aλ^4-trithiapentalene is roughly the same as the one obtained by Gleiter and Hoffmann from extended Hückel calculations Fig. 8.

Fabian[109] has by using HMO-LCI methods studied the absorption spectra of a series of trithiapentalenes.

Klingsberg[110] has pointed out that the no-bond resonance scheme used to describe the trithiapentalenes can be considered as a degenerate case of a rearrangement described by Katritzky and Boulton[111a] who have studied the general rearrangement 74A→74B.

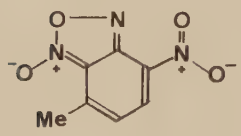


74A



74B

An example of such a rearrangement is 75→76 in the



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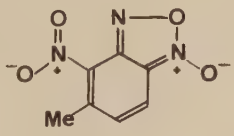

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nitrobenzofuroxane chemistry. The symmetrical structure in the trithiapentalenes corresponds to the transition state in the

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109 J. Fabian, Z. Chem. 13, 26 (1973).

110 E. Klingsberg, J. Heterocyclic Chem. 9, S-19 (1972).

111a A. J. Boulton and A. R. Katritzky, Proc. Chem. Soc. 257 (1962).

Katritzky-Boulton rearrangement in contrast to the nitrobenzofuroxane case where it is the unsymmetrical structure which is stable.

Clark[72] has calculated by ab initio methods the total energies for trithiapentalene in the symmetrical and the unsymmetrical case.

Symmetrical	-1368.220680 au
Unsymmetrical	-1368.220676 au

On the basis of this he proposes that the concept of no-bond resonance ought to be given up as there is no drastic change in the bonding pattern on distorting a symmetrical system to an unsymmetrical one within the range of S..S distances encountered in trithiapentalenes. Clark finds it more realistic to discuss the bonding problem in terms of a single or a double minimum energy curve for the S..S..S system, but we need more experimental and theoretical data before we know if we have to deal with a single or a double minimum. There may also be serious problems in using different spectroscopic techniques since questions of time-scale of measurement arise, and also the question whether the property investigated is essentially a ground state property or not need to be asked.

Clark has also discussed the d orbital participation on sulfur and he has found only a small contribution of d orbital as seen from table 7.

Palmer and Findlay[37,111b] have by use of gaussian orbital (LCGO) approach to the Hartree-Fock method on 1,6,6aλ^4-trithiapentalene and some oxa- and aza-derivatives come to the conclusion, that the molecules have only little resonance energy and that the 3d orbitals on the central sulfur atom are not heavily involved in the bonding in these compounds.

111b M. H. Palmer and R. H. Findlay, J. C. S. Perkin II 1885 (1974).

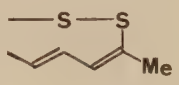
Table 7

Atom	Valence electron populations in 41[72]							
	σ		π		d		Total	
	Ab initio	CNDO	Ab initio	CNDO	Ab initio	CNDO	Ab initio	CNDO
S6a	4.308	4.282	1.870	1.753	0.598	0.682	6.178	6.035
S1,S6	4.407	4.319	1.761	1.803	0.220	0.345	6.169	6.122
C3a	3.039	3.059	0.786	0.830	-	-	3.825	3.889
C2(C5)	3.096	3.097	0.820	0.862	-	-	3.916	3.959
C3(C4)	2.957	2.949	1.091	1.044	-	-	4.048	3.993

8. NMR Spectroscopy.

Although ^1H chemical shifts are given in many papers dealing with synthesis and reactions of trithiapentalenes (for a collection of characteristic chemical shifts cf. ref. 5), only few papers dealing with the analysis of the NMR spectra have been published.

By comparison of the chemical shift of the methyl protons in 2,5-dimethyl-1,6,6aλ^4-trithiapentalene and 2-methyl naphthalene and the hypothetical model 77 it was concluded[112]



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that the aromaticity of the trithiapentalene was 65% of that of naphthalene. Dingwall et al[113] also conclude on the basis of ^1H chemical shifts, that the trithiapentalene is an aromatic system. ^1H chemical shifts and coupling constants for

Table 8 ^1H NMR Data for 1,6,6aλ^4-Trithiapentalene[114] and for Napthalene

	41	Naphthalene exp.	Naphthalene[c,d] calc.
$\delta_{H(2)}$	549·29 Hz		
$\delta_{H(3)}$	476·42 Hz		
^3J(H-2H-3)	+6·31 Hz	8·28[a]	
^5J(H-2H-4)	+0·08 Hz	+0·21[b]	+0·54
^6J(H-2H-5)	|0·345[e]|	-(0·2-0-3)[a]	0·02
^4J(H-3H-4)	|0·299[e]|	unobserved	-0·58

a J. B. Pawliczek and H. Günther, Tetrahedron 26, 1755 (1970).
b M. W. Jarvis and A. G. Moritz, Australian J. Chem. 24, 89 (1971).
c G. F. Adams, J. Phys. Chem. 75 3765 (1971).
d INDO finite perturbation calculation.
e This value may be interchanged.

112 R. Pinel, Y. Mollier and N. Lozac'h, Bull. Soc. Chim. Fr. 856 (1967).

113 J. G. Dingwall, S. McKenzie and D. H. Reid, J. Chem. Soc. C 2543 (1968).

1,6,6aλ^4-trithiapentalene are given in table 8[114].

The problem whether the trithiapentalene system has to be considered a mixture of the rapidly interconverting valence tautomers 40, 41 and 42 or whether these formulas should only be considered canonical structures of the same compound has been discussed by Pedersen and Schaumburg[114] on the basis of ^{13}C chemical shifts and relaxation times for the carbon skeleton in unsubstituted and substituted 1,6,6aλ^4-trithiapentalenes. If we had to deal with a 1,2-dithiolylidene thione structure such as 40 or 42, one should expect C(3a) to have a chemical shift near that of C(2) in 2-methyl thiophene, but the chemical shifts observed are quite different:

$C(3a)_{\text{trithiapentalene}}$: $\delta = 177$ ppm

$C(2)_{\text{2-methyl thiophene}}$: $\delta = 139.2$ -

If an interconversion between 40 and 42 takes place, we would expect the relaxation time for C(2) and C(3) in trithiapentalene to be different as this interconversion should be equivalent to the existence of a fast averaging of C(2)'s chemical shift over two very different values. This process, if operating, would contribute through chemical shift modulation to the relaxation process of C(2), whereas this effect will not be operative in the case of C(3). The following relaxation times have been observed:

C(2) : $T_1 = 7.2$ sec

C(3) $T_1 = 10.1$ -

These are both close to other data for small aromatic systems. This seems to be in accordance with the formulation of trithiapentalenes as aromatic bicyclic systems.

If the ^{13}C chemical shifts in trithiapentalenes are correlated with the charge of the respective carbon atoms a straight line is obtained which is in accordance with corresponding plots carried out for naphthalene. Fig. 11

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[114] C. Th. Pedersen and K. Schaumburg, Org. Magn. Resonance 6, 586 (1975).

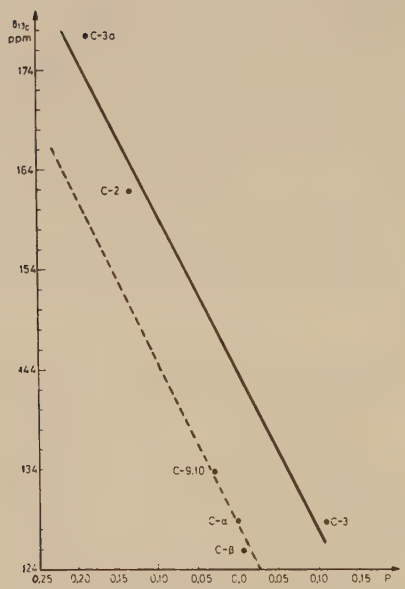

Fig. 11. Correlation of charge densities calculated using CNDO/2 and C-13 chemical shifts. The dotted line is the correlation for substituted benzenes from G.L. Nelson et al J. Amer.Chem.Soc. 94, 3089 (1972). C-α, C-β and C-9,10 are naphthalene data taken from A. J. Jones et al J. Amer. Chem. Soc. 92, 2386 (1970). The solid line is the correlation for 1,6,6aλ^4-trithiapentalene (ref. 114).

Lapper and Pool[115] have reached the same conclusion concerning the structure of trithiapentalenes by a study of the substituent chemical shift effect.

In table 8 is given some characteristic ^{13}C chemical shifts of substituted trithiapentalenes.

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[115] R. D. Lapper and A. J. Poole, Tetrahedron Letters 2783 (1974).

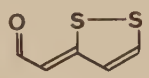
Table 8. ^{13}C Chemical Shift and $^{1}J(CH)$ Coupling Constants Observed in 1,6,6aλ^4-Trithiapentalenes. 49[114]

Substituent				Ref.	^{13}C chemical shift					^{1}J coupling constants	
R_1	R_2	R_3	R_4		C-2	C-3	C-4	C-5	C-3a		
H	H	H	H	114	161·69	128·64	128·64	161·69	177·45	C-2:	176·16
										C-3	165·3
CH_3	H	H	CH_3	-	176·78	126·94	126·94	176·78	178·91	C-3	160·0
CH_3	H	H	H	115	176·6	126·4	128·9	161·5	177·9		
Ph	H	H	CH_3	114	177·0	124·14	128·48	176·9	179·70		
Ph	H	H	Ph	-	175·66	124·84	124·84	175·66	177·0		
H	Ph	H	Ph	-	158·48	142·57	126·19	176·48	177·65	C-2	176·16
										C-4	163·74
H	H	Ph	Ph	-	168.7	127·65	140·8	168·9	177·30		
Ph	H	Ph	Ph	-	-	127·37	-	-	-		
$PhOCH_3$	H	$PhOCH_3$	$PhOCH_3$	-	180·92	125·90	138·84	180·92	179·11		
Ph	Ph	Ph	Ph	-	-	139·42	139·42	-	-		
Ph	H	H	H	115	176·1	125·5	127·4	160·9	177·9		
CH_3	H	Ph	H	-	176·3	127·6	141·4	158·7	178·6		
C_6H_5	H	H	SCH_3	-	165·6	122·1	124·2	190·9	174·0		
SC_2H_5	H	H	SC_2H_5	-	177·6	122·4	122·4	177·6	174·0		

IV α-(1,2-Dithiol-3-ylidene) ketones and aldehydes.

1. Introduction.

Dithiolylidene ketones can in the same way as trithiapentalenes be considered as hybrids of several canonical forms such as 78, 79 and 80.



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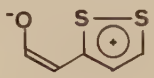

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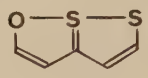

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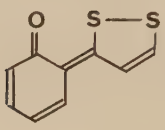
The compounds can be given different names corresponding to these resonance forms, e.g. 81, 82 and 83.



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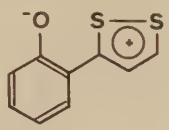

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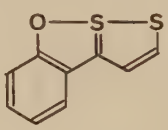

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81 : 6-(1,2-dithiol-3-ylidene)-2,6-cyclohexadien-1-one.

82 : 2-(1,2-Dithiol-3-ylio)phenolate.

83 : 8-oxa-1,8aλ^4-dithiacyclopenta[a]indene.

The name furothiophthene is also used in the literature.

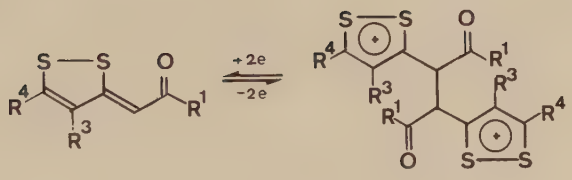
In this review we will use names corresponding to 81.

2. Electrochemistry.

One electron oxidation of 84 gave the dimeric cation 85[116a,116b].

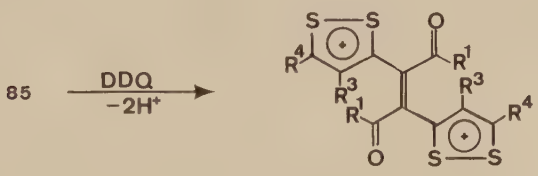
116a O. Hammerich, V. D. Parker and C. Th. Pedersen, Acta Chem. Scand. B30 (1976) in press.

116b C. Th. Pedersen, O. Hammerich and V. D. Parker, Int. J. Sulfur Chem. A2, 195 (1972).



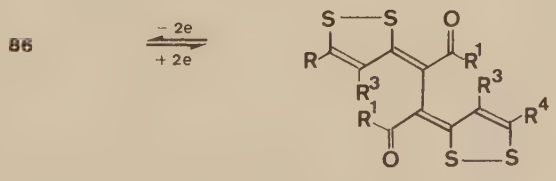
84 85

85 was not capable of undergoing further electrochemical oxidation, but treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave rise to a new dication 86, which upon elec-



86

trochemical reduction gave the dimer 87 of the original dithiolylidene ketone 84.



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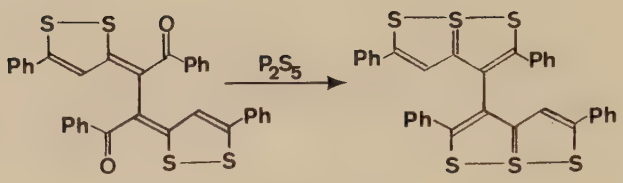
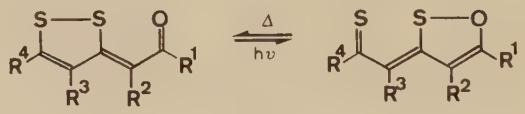
The dimer 87 could be converted into the dimeric 4-trithiapentalene 89 by reaction with phosphorus pentasulfi



88 89

3. Photochemistry.

It was observed by Gleiter et al[117] that 1,2-dithiolylidene ketones 90 were transformed into a photoproduct upon irradiation. The photoproduct reverted to starting material by a dark process. Gleiter ascribed the O-S bonded structure 91 to the photoproduct.



90 91

Pedersen and Lohse[118,119] have, however, shown that the product formed is in fact the isomeric trans dithiolylidene ketone 92, which is in accordance with the HSAB principle[119a].

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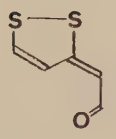
[117] R. Gleiter, D. Werthemann and H. Behringer, J. Amer. Chem. Soc. 94, 651 (1972).

[118] C. Th. Pedersen and C. Lohse, Chem. Comm. 123 (1973).

[119] C. Th. Pedersen and C. Lohse, J. C. S. Perkin I 2837 (1973).

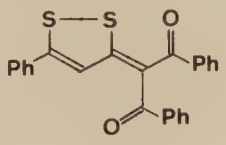
[119a] Tse-Lok Ho, Chem. Rev. 75, 1 (1975).



92

If the dithiolylidene ketones were irradiated in a methacrylic matrix they were converted into a photoproduct, but they only reverted to starting material upon prolonged heating. This is consistent with the formation of a trans form as the conversion from trans to cis is a drastic geometric change and therefore it should be strongly dependent on the viscosity of the solvent.

The formation of a trans form was further confirmed by the observation that no photoisomerization was observed upon irradiation of 93[119] as the cis form in this case is identical with the trans form.



93

Calzaferri et al[120] have studied the NMR and IR spectra of the photoproducts. They have found the following values for the carbonyl vibration.

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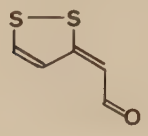
120 G. Calzaferri, R. Gleiter, K.-H. Knauer, E. Rommel, E. Schmidt and H. Behringer, Helv. Chim. Acta 56, 597 (1973).

Table 9[120]

	ν_{CO} start.	ν_{CO} photopr.
α-(5-Methyl-1,2-dithiol-3-ylidene)acetone	1595 cm^{-1}	1645 cm^{-1}
α-(5-Phenyl-1,2-dithiol-3-ylidene)acetophenone	1552 cm^{-1}	1635 cm^{-1}

There may be several possibilities 94, 95 and 92 for the structure of the S-S bonded photoproducts.



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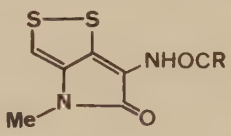
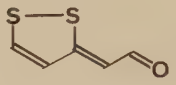


94A



95

The ^{1}H NMR data and the substituent effect are consistent with the conformation 92. The conformation 94 is found in a "frozen form" in a series of antibiotics, thiolutin, aureothricin, isobutyropyrrothine and holomycin[120a, b, c, d] isolated from various Streptomyces species. They all have the general formula 94A with various R groups.

Comparison of IR carbonyl vibrations of ^{16}O and ^{18}O enriched compounds shows that in the cis form there is only 20% ketonic contribution due to polar forms whereas the contribution is as high as 57% in the photoproduct.

The electronic spectra of the cis and trans forms are very similar[120,121].

The rate constants for a series of compounds are given in table 10.

120a U. Schmidt and F. Geiger, Angew. Chem. 74 328 (1962).

120b U. Schmidt and G. Geiger, Ann. 664 168 (1963).

120c B. Büchi and G. Lukas, J. Amer. Chem. Soc. 86 5654 (1964).

120d B. Jensen, Acta Cryst. B27, 392 (1971).

121 R. Gleiter, K.-H. Knauer, E. Schmidt, Y. Mollier and R. Pinel, Tetrahedron Letters 1257 (1973).

Table 10

Rate Constants for Thermal trans-cis-Isomerization of Compounds 90[119]

R_1	R_2	R_3	R_4	k_{EtOH}/s^{-1} *
Ph	H	H	Ph	3.1×10^{-3}
Ph	H	H	4-$MeOC_6H_4$	9.6×10^{-3}
Me	H	H	Ph^6H_4	5.7×10^{-3}
Ph	H	Me	Me	3.1×10^{-3}
Me	H	H	Me	9.5×10^{-3}
Ph	H	Ph	H	3.6×10^{2}
Ph	H	Ph	Ph	5.0×10^{2}
4-MeC_6H_4	H	Ph	Ph	2.9×10^{2}
4-BrC_6H_4	H	Ph	Ph	10.6×10^{2}
Ph	Ph	Ph	Ph	2.6
Ph	Ph	Ph	H	2.5
Ph	Ph	4-$MeOC_6H_4$	4-$MeOC_6H_4$	10.3
4-$MeOC_6H_4$	4-$MeOC_6H_4$	Ph^6H_4	Ph^6H_4	0.35
H	Ph^6H_4	Ph	Ph	45
H	H	Ph	Ph	4.3
H	Ph	H	Ph	2×10^{-2}

* Rate constants for the thermal back reaction from 10^{-5}M solutions in absolute ethanol.

Calzaferri has from kinetic measurements estimated that there should be a difference in stability of 15 kcal/mole between the cis and trans isomer. This is in good agreement with CNDO/2 calculations[122] which give a value of 20 kcal/mole for this difference if d orbitals are taken into consideration.

4. Mass Spectrometry.

1,2-Dithiol-3-ylidene ketones and aldehydes normally give mass spectra with intense molecular ions[123]. Other intense peaks are due to the loss of acylium ions. In some cases,

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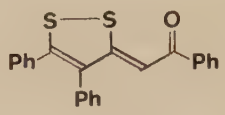
122 R. Pinel, Y. Mollier, J.-P. de Barbeyrac and G. Pfister-Guillouzo, C. R. Acad. Sci. Paris 275 (C), 909 (1972).

123 C. Th. Pedersen, N. L. Huaman, R. Pinel and J. Møller, Acta Chem. Scand. 26, 1305 (1972).

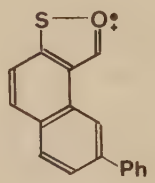
e.g. 96, it was observed that neutral acyl radicals were



96

expelled with charge retention on the dithiole moiety, probably due to the great ability of the dithiole nucleus to stabilize a positive charge.

Loss of OH gives rise to ions with the same structure as 57, which is derived from trithiapentalenes by expulsion of SH. Loss of SH from dithiolylidene ketones and aldehydes gives rise to the analogous ion 97.

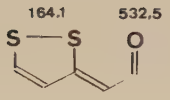


97

5. ESCA and photoelectron spectroscopy.

Lindberg et al[29] have studied the ESCA spectra of a series of 1,2-dithiolylidene ketones and aldehydes.

Calculated core binding energies in eV for sulfur and oxygen in structures which may be considered for this class of compounds are given below. The average sulfur shift observed for a series of compounds is 164.1 eV and the average oxygen shift is 531.1 eV, which means that the oxygen is considerable more negative than normal carbonyl oxygen. The negative character



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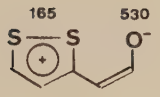

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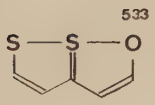

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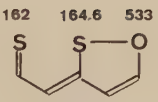

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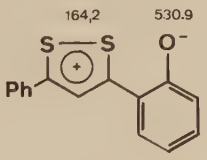
of the oxygen does not seem to be consistent with any considerable pπ-dπ bonding interaction between oxygen and sulfur. The shifts observed are in good agreement with those calculated for the structure 79.

The average shifts are also very close to those observed for the true zwitter-ionic compound 99.



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6. Structure Determinations.

Relatively few structure determinations have been carried out on 1,2-dithiolylidene ketones and aldehydes; cf. Table 11.

Table 11.

S-S and S-O Distances in 1,2-Dithiolylidene Ketones 90

				S(1)-S(2)	S(2)-O	Ref
Me	H	H	Me	2.12	2.41	48
Ph	H	Ph	H	2.106	2.382	124
4-Me_2NPh	H	Ph	H	2.101 2.111	2.443 2.284	125
-$CH_2CH_2CH_2CH_2$		H	Ph	2.126	2.255	126

In all compounds S..O distances less than the sum of the van der Waal radii are observed. Pinel and Mollier[126] have discussed the correlation between the IR spectra (carbonyl vibration) and S..O distances and have concluded that the S..O distance is an intrinsic molecular property rather than a consequence of crystal forces. In this connection is has to be noticed that the S..O distances in the two crystallographically independent molecules of 100 are different[125].

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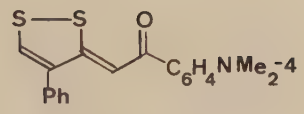
124 A. Hordvik, E. Sletten and J. Sletten, Acta Chem. Scand. 23, 1377 (1969).

125 A. Hordvik and L. J. Sæthre, Acta Chem. Scand. 26, 849 (1972).

126 R. Pinel, Y. Mollier, E. C. Llaguno and I. C. Paul, Chem. Comm. 1352 (1971).



100

Leung and Nyburg[127] have pointed out that there is a correlation between the differences in the electronenegativity of S and X in the system S..S..X and the S..S bond lenght in such a way that the S..S distance decreases as the difference in electronenegativity increases.

7. NMR Spectrscopy.

Lindberg et al[128] have studied the correlation between $\delta^{19}F$ values and the S2p binding energies obtained from ESCA spectra and have found a linear correlation for 101, 102 and some other 1,2-dithiole derivatives. This shows that the ^{19}F chemical shifts in the case of 1,2-dithiole derivatives constitute a convenient evaluation of the charge.

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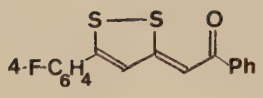
127 F. Leung and S. C. Nyburg, Can. J. Chem. 49, 167 (1971).

128 B. J. Lindberg, R. Pinel and Y. Mollier, Tetrahedron, 30, 2537 (1974).



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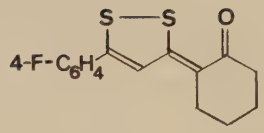

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8. Infrared Spectroscopy.

It was already observed by Guillouzo[47] that 1,2-dithiolylidene ketones did not display a normal carbonyl vibration in the 1610-1750cm^{-1} where most carbonyl compounds absorb.

The infrared spectra of dithiolylidene ketones have been studied intensively by Mollier and collaborators[129-132].

By comparison of the IR spectra of ^{16}O compounds with those of ^{18}O enriched compounds it was possible to locate the carbonyl vibration.

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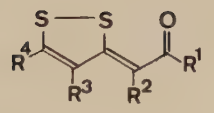
129 D. Festal and Y. Mollier, Tetrahedron Letters, 1259 (1970).

130 R. Pinel and Y. Mollier, Bull. Soc. Chim. Fr. 1385 (1972).

131 E. C. Llaguno, I. C. Paul, R. Pinel and Y. Mollier, Tetrahedron Letters, 4687 (1972).

132 D. Festal, J. Tison, N. Kim Son, R. Pinel and Y. Mollier, Bull. Soc. Chim. Fr. 3339 (1973).



103 R^1:Ph, R^2:CN, R^3:H, R^4:Bu^t

104	Ph	CN	H	DMAPh-4
105	Me	H	H	Ph

103: ν_{CO} = 1554 (s)
104: ν_{CO} = 1549 (s)
105: ν_{CO} = 1574 (s)

By this method it could be shown that a band at 1460 cm^{-1} originally ascribed to the carbonyl vibration[133] had nothing to do with the carbonyl group.

From the isotopic displacement of the carbonyl vibration the contribution of true ketonic structure in the dithiolylidene ketones could be calculated. The values obtained are found in Table 12.

Table 12

Observed and calculated isotopic displacements[129].

Ketone	$\Delta\nu(cm^{-1})$ obs.	calc.	% participation of ν_{CO}
ω-Cyanacetophenone.	32	41	78
α-(4-Phenyl-[1,2-dithiol-3-yl])acetone.	30	41.4	73
α-(4-Phenyl-[1,2-dithiol-3-ylidene])acetone.	12	37.3	34
α-(5-t-Butyl-[1,2-dithiol-3-ylidene]) cyanacetophenone.	14	37.4	38
α-(5-p-Toty1-[1,2-dithiol-3-ylidene]) cyanacetophenone.	10	37.3	27

133 F. Bohlmann and E. Bressinsky, Chem. Ber. 93, 1566 (1960).

As can be seen there is a relatively important difference between the calculated and observed displacement. This is due to the contribution of polar forms such as 79.

9. Theoretical studies.

Whereas the stucture of 1,6,6aλ^4-trithiapentalenes has been the subject of several theoretical papers, the corresponding oxygen analogues have only been little discussed.

In connection with extended Hückel calculations on compounds with a short S..O distance the charge densities in α-(4-methyl-1,2-dithiol-3-ylidene)acetone have been calculated[134]. It was the result of this study that if present the covalent bonding between oxygen and sulfur is only weak and there is some doubt about the direct correlation of short interatomic distances between formally nonbonded atoms and partial single bonds.

These conclusions are not in accord with the calculations by Pfister-Guillouzo[122,135,136] who has used CNDO/2 methods with inclusion of d-orbitals on sulfur. These calculations show a great contribution of sulfur d-orbitals. The result of these calculations is that there has been created a bond between sulfur and oxygen as if a pair of electrons had been transfered from oxygen to the d-orbitals of the central sulfur atom. The pπ-dπ interaction, however, is only small between sulfur and oxygen.

The relative stability of 106 and 107 has also been calculated by CNDO/2 methods and the results shown in Table 13 were obtained

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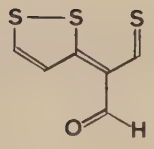
134 J. A. Kapecki and J. E. Baldwin, J. Amer, Chem. Soc, 91, 1120 (1969).

135 J. P. de Barbeyrac, D. Conbeau and G. Pfister-Guillouzo, J. Mol. Structure, 16, 103 (1973).

136 J. P. de Barbeyrac, D, Conbeau and G. Pfister-Guillouzo, J. Mol. Structure, 16, 117 (1973).



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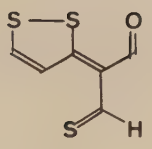

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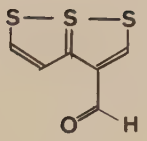

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Table 13.[136]

Compound	Conformation	Method	Electronic energy (a.u)	Total energy (a.u.)	ΔE Total energy (kcal mole^{-1})
106	CO trans	without d orbitals	-331.5065	-96.1038	-12.5
107	CS trans	without d orbitals	-333.2862	-96.0665	
107	CS cis	without d orbitals	-329.5726	-96.0837	
106	CO trans	with d orbitals on central sulfur	-331.8526	-96.4499	-44.5
107	CS trans	with d orbitals on central sulfur	-335.5858	-96.3611	
107	CS cis	with d orbitals on central sulfur	-329.8675	-96.3785	

As can be seen structure 106, which corresponds to the trithiapentalene structure 108, is strongly favoured over the dithiolylidene aldehyde structure.

These observations are in accord with the rate constants observed for the thermal reversal of the photoproducts formed from 1,2-dithiolylidene ketones[119] and trithiapentalenes[57].

For α-(1,2-dithiol-3-ylidene)acetaldehyde it has been calculated[122] that the cis form is favoured by 20 kcal/mole if d orbitals are included and 4.4 kcal/mole if d orbitals are excluded.

Yamabe et al[100] have made ASMO SCF calculations on α-(4-methyl-1,2-dithiol-3-ylidene)acetone, but the calculated electronic transition energies do not match experimental values particularly well.

V. Extended Structures.

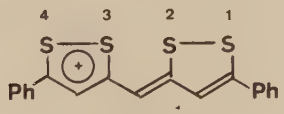
1. Introduction.

The trithiapentalene system embodies a structural principle that is capable of indefinite extension. Repetition of the vinylenethio group -CH=CH-S gives rise to a succession of higher polycyclic systems each composed of dithiole rings. The members of this family with an even number of sulfur atoms will be cations and those which have an odd number of sulfur atoms will be neutral compounds.

Until now, however, it has only been possible to extend the system to compounds with four and five sulfur atoms. Only few papers dealing with the physico chemical aspects of these classes of compounds have been published.

2. 3-(1,2-Dithiol-3-ylidenemethyl)-1,2-dithiolylium salts.

The first member 109 of this class was synthesized by



109

Klingsberg[137]. The structure has been determined by Hordvik[138]

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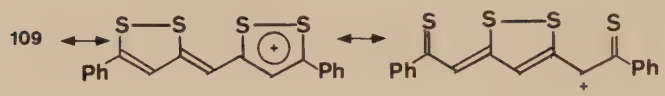
[137] E. Klingsberg, J. Heterocyclic Chem. 3, 243 (1966).

[138] A. Hordvik, Acta Chem. Scand. 19, 1253 (1965).

who found the S..S distances:

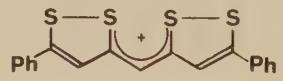
S(1)-S(2) = 2.03 Å
S(2)-S(3) = 2.93 Å
S(3)-S(4) = 2.00 Å

(cf. ref. 141). Several resonance structures, e.g. 109, 110 and 111, can be written for these compounds.



110 111

The X-ray data, however, show that there can only be a weak interaction between the two central sulfur atoms which means that structures such as 111 has only little weight. The identical sulfur distances between the outer sulfur atoms and the observation that the two dithiole protons are equivalent in the NMR spectra[139], show the symmetrical nature of the system, which can be explained by structures such as 112.



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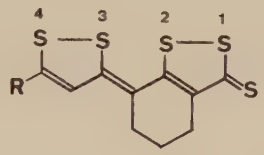
139 C. Lemarie-Retour, M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr. 1659 (1973).

3,7-(1,2-Dithiol-3-ylidene)-4,5,6,7-tetrahydro-1,2-benzodithiole-3-thiones.

Compounds of type 113 were synthesized by Stavaux and Lozac'h[140].



113

114 R: Bu^t

The cyclohexane ring is a prerequisite for the synthesis of compounds of this type.

The structure has been determined by Sletten[141] who in 114 has found the following sulfur distances:

S(1)-S(2) = 2.062 Å
S(2)-S(3) = 2.863 Å
S(3)-S(4) = 2.063 Å

S(1)--S(2)--S(3) is aproximately linear while the fourth sulfur atom deviates significantly from this line, the angle S(1), S(2), S(3) / S(3), S(4) being 163°. The two outer sulfurdistances are not significantly different from those in isolated disulfide rings. 3-Phenyl-1,2-dithiolylium iodide[142] for instance has a S..S = 2.00 Å. From the C-S bondlengths in

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140 M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr. 4423 (1971).

141 J. Sletten, Acta Chem. Scand. 26, 873 (1972).

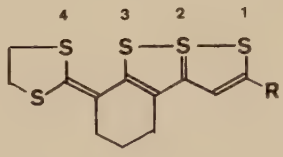
142 A. Hordvik and H. M. Kjøge, Acta Chem. Scand. 19, 935 (1965).

114 it can be judged that there is a comparable π-conjugation in the two dithiole rings.

The mass spectra of compounds of type 113 are dominated by strong molecular ions which are the base peaks[143].

4.4a,5-[1-(1,3-Dithiolan-2-ylidene)-tetramethylene]-1,6,6aλ^4-trithiapentalene.

Compounds of type 115 have been described by Stavaux and Lozac'h[144].



116 R: Bu^t
117 R: An

115

Structure determination has been carried out by Sletten[145] who has found the following sulfur distances:

S(1)-S(2) = 2.482 Å
S(2)-S(3) = 2.209 Å
S(3)-S(4) = 2.965 Å

On the basis of the S..S bonds it is proposed that S(1), S(2) and S(3) are parts of a true trithiapentalene system

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143 C. Th. Pedersen, M. Stavaux and J. Møller, Acta Chem. Scand. 26, 3875 (1972).

144 M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr. 4419 (1971).

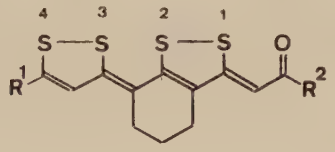
145 J. Sletten, Acta Chem. Scand. 27, 229 (1973).

whereas S(4), although S(3)-S(4) is shorter than the sum of the van der Waal radii, does not participate in σ-bonding to S(3).

The crystals of 117 are found to consist of two chemically equivalent but crystallographically different molecules with different sulfur-sulfur distances[146].

5. α-[7-(1,2-Dithiol-3-ylidene)-4,5,6,7-tetrahydro-1,2-benzodithiol-3-ylidene] ketones.

The formation of the compounds 118, which are analogous to 1,2-dithiolylidene ketones, has been described by Stavaux[147].



118

119 R^1: Bu^t
R^2: Ph

The following distances have been determined by Sletten and Velsvik[148] for 119.

S(1)-S(2) = 2.110 Å
S(2)-S(3) = 2.856 Å
S(3)-S(4) = 2.064 Å
S(1)-O = 2.327 Å

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146 J. Sletten, Acta Chem. Scand. A28, 499 (1974).

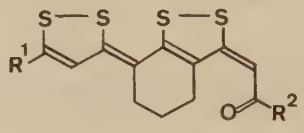
147 M. Stavaux, Bull. Soc. Chim. Fr. 4429 (1971).

148 J. Sletten and M. Velsvik, Acta Chem. Scand. 27, 3881 (1973).

This compound is similar to 114, but we see that the introduction of the oxygen atom gives a pronounced lengthening of the S-S bond adjacent to the oxygen whereas the other S..S bond is not changed. This indicates that a delocalized σ-system does not include all the five atoms in the linear row. From the S(4)..O bond distance it can be estimated that a significant interaction is present between these two atoms.

The mass spectra of compounds of type 118[143] display intense molecular ion peaks, other prominent peaks in the spectra are due to acyl ions R^2CO^+ and to ions resulting from loss of neutral acyl radicals with charge retention on the rest of the molecule.

The photochemistry of 118 has been studied by Pedersen et al[149]. It is found that these compounds are transformed into trans form 120 upon irradiation. The trans forms revert to cis in a dark process on the same way as observed for 1,2-dithiolylidene ketones. Isomerization round the other exocyclic double bond was not observed.



120

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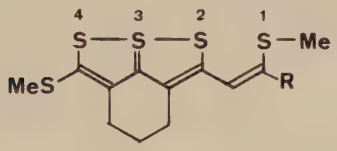
149 C. Th. Pedersen, C. Lohse and M. Stavaux, J. C. S. Perkin I, 2722 (1974).

6. 2-(2-Methylthiovinyl)-3,4-trimethylene-5-methylthio-1,6,6aλ^4-trithiapentalenes.

Compounds of type 121 have been described by Stavaux



121

122 R: An

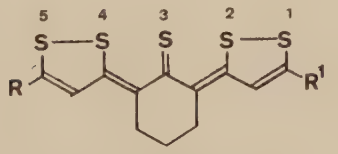
and Lozac'h[144]. Structure determination has been carried out by Sletten[150]. She has found the following S..S distances in 122:

S(1)-S(2) = 3.0021 Å
S(2)-S(3) = 2.1563 Å
S(3)-S(4) = 2.5510 Å

The values obtained for this compound are close to those found for 116 and 117.

7. 2,6-Bis-(1,2-dithiol-3-ylidene)cyclohexanethiones.

Stavaux[147] has prepared compounds with the general formula 123. The symmetry of the molecule is consistent with



123

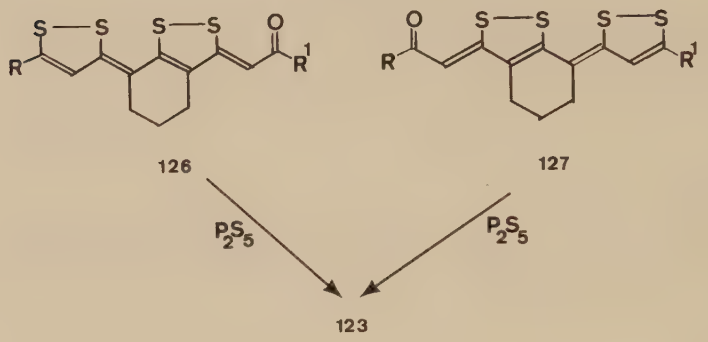
124 R=R¹=Bu^t

125 R:Bu^t, R¹: Ph

150 J. Sletten, Acta Chem. Scand. 27, 229 (1973).

the observation that if R=R' as in 124, the two substituents R and R' give identical ^{1}H NMR signals and the dithiole protons are also identical.

Stavaux has shown that the same compound 123 is obtained from the two different oxygen analogues 126 and 127.



This seems to imply that a reorganization of the bonds takes place during the sulfuration with formation of a symmetrical system, which may be described with the classical formula 123.

X-ray studies carried out by Kristensen and Sletten[151,152a] show that the 5 sulfur atoms are approximately linear. The following S..S distances have been found:

	124	125
S(1)-S(2)	2.183 Å	2.14 Å
S(2)-S(3)	2.580 Å	2.62 Å
S(3)-S(4)	2.583 Å	2.55 Å
S(4)-S(5)	2.172 Å	2.16 Å

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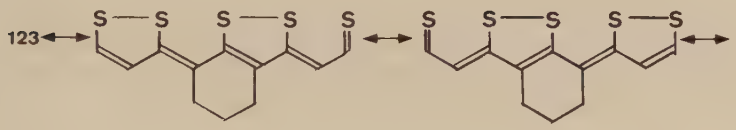
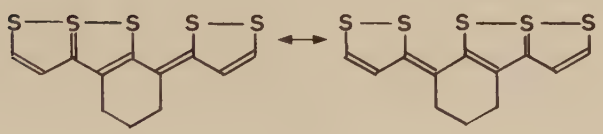
151 J. Sletten, Acta Chem. Scand. 24, 1464 (1970).

152a R. Kristensen and J. Sletten, Acta Chem. Scand. 27, 2517 (1973).

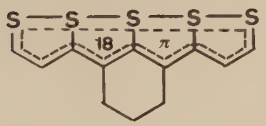
The distances observed seem to indicate that both σ- and π-delocalization over all the five sulfur atoms are present. This is consistent with the hypothesis that we have to deal with a trithiapentalene structure which can be described by the resonance forms 123, 128 and 129 where d orbitals on sulfur are not involved and 130-132 which involve d orbital participation on sulfur.



128 129



130 131



132

The NMR data are also consistent with π conjugation, the dithiole protons are found in the range δ 7.04 - 7.37 ppm which should be compared with the δ value for the hydrogens in benzene 7.27 ppm.

These compounds show absorption in the visible and ultraviolet regions which are similar to those of trithiapen-

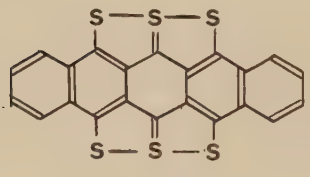
talenes, the absorption bands are only shifted a little towards a longer wavelength. It is possible that the visible absorption in this case, as proposed for the corresponding bands in trithiapentalenes, is due to $\pi \rightarrow \pi^*$ transitions[99].

Thus, in the same way as the sulfur-sulfur σ bonding in trithiapentalenes is described as a "4-electron 3-center bond"[108], the corresponding bond in this type of compound may be described as a "6-electron 5-center bond".

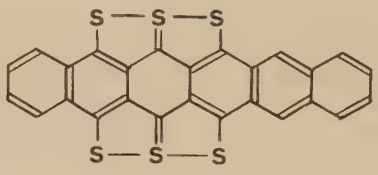
The mass spectra of these compounds[143] display intense molecular ions as well as peaks corresponding to thioacyl ions RCS^+. Ions corresponding to loss of 1,2,3 and 4 sulfur atoms from the molecular ion are also present.

8. Pentacene Hexasulfide.

Pentacene hexasulfide 132A[152b] is an example of a type of trithiapentalene which can be considered extended



132A



132B

1,2-dithiolederivatives, in this case the conjugation between the different 1,2-dithiole moities is established through a carbocyclic aromatic system. The corresponding hexacene hexasulfide 132B is also known. Pentacene hexasulfide is an insulator with a conductivity of $1.2 \times 10^{-13}\ \Omega^{-1}cm^{-1}$, whereas hexa-

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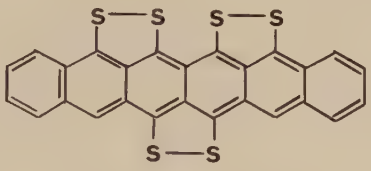
152b E. P. Goodings, D. A. Mitchard and G. Owen, J. C. S. Perkin I, 1310 (1972).

cene hexasulfide has the unusual high electrical conductivity of $8.3 \times 10^{-5}\ \Omega^{-1}cm^{-1}$. This is rather surprisingly as 132A and 132B only differ in the annelation of a benzene ring. As the authors have not given any proof of structure it is possible that the large difference in conductivity is due to a greater variation in molecular structure e.g. 132C or structures with partial bonds between the sulfur atoms.



132C

Corresponding anthracene derivatives have recently been described by Leaver and his group[152c].

152c S. Davidson, D. Leaver and J. H. Steven. Proccedings of the VI International Symposium on Organic Sulphur Chemistry. D21 (1974).

VI. Trithiapentalene analogues.

1. Introduction.

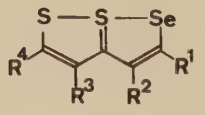
In principle, two different types of trithiapentalene analogues exist. Compounds where one or more of the sulfur atoms have been replaced by O, Se or N-R is one group, the other consists of compounds where one or more carbon atoms are replaced by nitrogen. A few compounds which are a mixture of these two have been described.

For the sake of brevity we will use bicyclic formulas and names analogous to trithiapentalene without any preconception of the electronic structure of these compounds, which for many of them is not known.

The 1,2-dithiole-3-ylidene ketones belong logically to this class of compounds, but have been treated in a separate chapter because of their near relationship to the trithiapentalene and the many papers dealing with such compounds.

2. 6-Selena,1,6aλ^4-dithiapentalenes.

Compounds of type 133 have been prepared by van den Hende and Klingsberg[153] and Dingwall et al[154] by different methods.



133

134 $R^1 = R^3 = H$
$R^2 = R^4 = Ph$

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153 J. H. van den Hende and E. Klingsberg, J. Amer. Chem. Soc. 88, 5045 (1966).

154 J. G. Dingwall, D. H. Reid and K. O. Wade, J. Chem. Soc. (C) 2543 (1968).

X-ray structure determination[153] has given the following values for the S..S and S..Se bonds in 134.

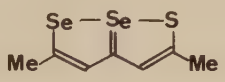
S..S = 2.492 Å

S..Se = 2.333 Å

The S..Se distance is longer than the normal covalent S-Se distance (2.21 Å) but shorter than the sum of the van der Walls radii (ca. 3.7 Å). The bondlengths seem to indicate the presence of a trithiapentalene like system. The UV-VIS spectrum of 134 is very much like the spectrum of the corresponding trithiapentalene[153].

3. 1-Thia-6,6aλ^4-diselenapentalene.

The dimethyl derivative 135 has been prepared by Traverso[155].



135

4. 1-Oxa-6,6aλ^4-diselenapentalenes.

The dimethyl derivative 136 was described by Sanesi and Traverso[156]. They have determined the dipolemoment to be 3.30 D.

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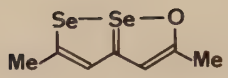
155 G. Traverso, Ann. Chim. (Rome), 47, 3 (1957).

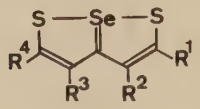
156 M. Sanesi and G. Traverso, Chem. Ber. 93, 1566 (1960).



136

5.1,6-Dithia-6aλ^4-selenapentalenes.

The parent compound 138 and substituted compounds have been prepared by Reid[157].



137

138 $R^1 = R^2 = R^3 = R^4 = H$

139 $R^1 = R^4 = H$, $R^2 = R^3 = Me$

140 $R^1 = R^4 = Ph$, $R^2 = R^3 = H$

^{1}H NMR studies by Reid of the parent compound and substituted compounds show that the compound in solution posses real or time averaged C_{2v} symmetry.

The structure of 138, 139 and 140 has been studied by X-ray chrystallography by Hordvik et al[158-60]. They have

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157 D. H. Reid, J. Chem. Soc. (C) 3187 (1971).

158 A. Hordvik and K. Julshamn, Acta Chem. Scand. 25, 1895 (1971).

159 A. Hordvik, T. S. Rimala and L. J. Sæthre, Acta Chem. Scand. 27, 360 (1973).

160 A. Hordvik, T. S. Rimala and L. J. Sæthre, Acta Chem. Scand. 26, 2139 (1972).

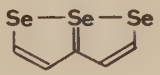
found the following S..Se distances.

	138	139	140
S(1)-Se(6a) =	2.446 Å	2.414 Å	2.419 Å
Se(6a)-S(6) =	2.446 Å	2.414 Å	2.433 Å

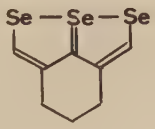
The two different S..Se distances in 140 are caused by a torsion of the phenyl groups out of the plane of the selenapentalene of 6° and 46°, respectively.

6.1,6,6aλ^4-Triselenapentalene.

The compounds 141 and 142 have been prepared by Jackson[161].



141



142

Hordvik et al[162,163] have determined the structure of 141 and 142. The following Se..Se distances have been observed:

	141	142
Se(1)-Se(6a) =	2.583 Å	2.568 Å
Se(6a)-Se(6) =	2.583 Å	2.554 Å

It is obvious from the X-ray data that the triselenapentalene system is much like the trithiapentalene system.

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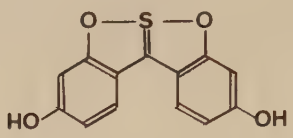
161 M. G. Jackson, PhD Thesis, University of St. Andrews 1973.

162 A. Hordvik and K. Juelshamn, Acta Chem. Scand. 25, 2507 (1971).

163 A. Hordvik and J. A. Porten, Acta Chem. Scand. 27, 485 (1973).

7. 1,6-Dioxa-6aλ^4-thiapentalenes.

The first representative 143 of this class of compounds was prepared by Pomerantz et al[164,165] by fusion



143

of the fungicide "Captan" with resorcinol. They give ^{1}H NMR data and mass- and ultraviolet-visible spectra for 143 and some of its derivatives.

The structure of the dimethyl ether of 143 was determined by X-ray crystallography by Gilardi and Karle[166].

O..S..O forms a nearly linear system with equivalent O..S distances of 1.879 Å which is much shorter than the shortest O..S distance found in dithiolylidene ketones[126] (2.255 Å), but it is still ca. 0.28 Å longer than the normal S-O single bond.

The existence of such compounds as 143 is very interesting as it has not been possible to prepare analogous dibenzotrithiapentalenes[167], probably because of steric interaction between the interior ortho protons in the benzene

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164 I. Pomerantz, L. J. Miller, E. Lustig, D. Mastbrook, E. Hansen, R. Barron, N. Oates and J.-Y. Chen, Tetrahedron Letters, 5307 (1969).

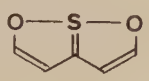
165 I. H. Pomerantz, L. J. Miller, R. Barron, E. Hansen, D. Mastbrook and I. Egry, Tetrahedron, 28, 2183 (1972).

166 R. D. Gilardi and I. L. Karle, Acta Cryst. B27, 1073 (1971).

167 E. Klingsberg, J. Org. Chem. 37, 3226 (1972).

rings. In 143 the distance between these two hydrogens is 2.02 Å, but if the two oxygens are changed to sulfur the two benzene rings will be forced nearer to each other.

The parent system 144 has been prepared by Reid[168].

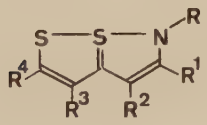


144

According to the ^{1}H NMR spectrum the compound retained C_{2v} symmetry down to -50°C.

8. 6-Aza-1,6aλ^{4}-dithiapentalenes.

Compounds of type 145 were first described by Klingsberg[169]



145

146 R: 3-Quinolinyl
$R^1 = R^3 = H$, $R^2 = R^4 = Ph$

147 $R = R^2 = R^4 = Ph$
$R^1 = R^3 = H$

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168 D. H. Reid and R. G. Webster, Chem. Comm. 1283 (1972).

169 E. Klingsberg, J. Org. Chem. 33, 2915 (1968).

Ultraviolet and visible spectral data have been given by Klingsberg and Behringer[170]. Reid and his group[171] have prepared a series of azadithiapentalenes and recorded ^{1}H NMR spectra. They find a progressive increase in deshielding of ring protons and substituents along the series 1-oxa-6,6aλ^4-dithiapentalene (dithiolylidene ketones) ——> 6-aza-1,6aλ^4-dithiapentalenes ——> 1,6,6aλ^4-trithiapentalenes. It can be estimated that the π delocalization increases in the same order.

Reid has found that the azadithiapentalenes as the only class of hypervalent sulfurcompounds of this type form stable charge transfer complexes with 1,3,5-trinitrobenzene.

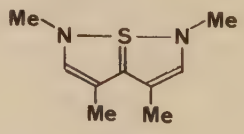
Leung and Nyburg[127,172] have determined the structure of 146 and 147 and found the following distances.

	146	147
N-S(6a) =	1.887 Å	1.871 Å
S(6a)-S(1) =	2.364 -	2.396 -

They also find that the bond N-C(5) = 1.324 Å resembles the one found in formamide which is 1.322 Å.

9. 1,6-Diaza-6aλ^4-thiapentalenes.

Compounds of type 148 have been prepared by Reid[173a].



148

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170 H. Behringer and J. Falkenberg, Chem. Ber. 102, 1580 (1969).

171 J. G. Dingwall, A. S. Ingram, D. H. Reid and J. D. Symon, J. C. S. Perkin I 2351 (1973).

172 F. Leung and S. C. Nyburg, Can. J. Chem. 50, 324 (1972).

173a D. H. Reid and J. D. Symon, Chem. Comm. 1314 (1969).

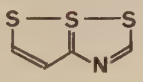
Reid has recorded the ^{1}H NMR spectrum of 148 and finds that the pattern of this spectrum, which show equivalence of C-Me,N-Me as well as of dithiolic protons, remained unchanged down to -70°C. This shows that the compound in solution has real or time averaged C_{2v} symmetry.

Hordvik and Julshamn[173b] have determined the structure of 1,6-dimethyl-3,4-trimethylene-1,6-diaza-6aλ^4-thiapentalene and found two values for the S..N bond length (1.901 Å and 1.948 Å). The C_{2v} symmetry is probably distorted in the anisotropic crystal state by intermolecular forces.

Reid and co-workers[173c] have recently prepared a series of substituted derivatives and have given ^{1}H NMR data. The compounds form charge transfer complexes with 2,4,6-trinitrobenzene.

10. 3-Aza-1,6,6aλ^4-trithiapentalenes.

Behringer and Bender[174] have described substituted



149

derivatives of 149. On the basis of UV-VIS spectra they conclude that the compounds are trithapentalene like.

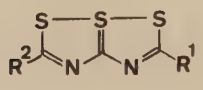
173b A. Hordvik and K. Julshamn, Acta Chem. Scand. 26, 343 (1972).

173c A. S. Ingram, D. H. Reid and J. D. Symon, J. C. S: Perkin I 242 (1974).

174 H. Behringer and D. Bender, Chem. Ber. 100, 4027 (1967).

11. 3,4-Diaza-1,6,6a-trithiapentalenes.

Behringer et al[175] have prepared 151 and Vialle et



150

151 $R^1 = R^2 = HNR$

152 $R^1 = R^2 = HNPh$

153 $R^1 = R^2 = Ph$

al[176] have described other substituted derivatives. The UV and VIS spectra are given by Behringer.

Hordvik has determined the structure of 152[177] and 153[178,179] and found the following S..S distances:

	152	153
S(1)-S(6a) =	2.225 Å	2.319 Å
S(6a)-S(6) =	2.475 -	2.328 -

The difference in S..S distances is caused by twisting of the phenyl groups. In 152 there is weak hydrogen bonding between the molecules in the crystal as shown in 154.

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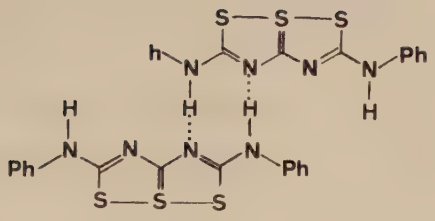
175 H. Behringer and D. Weber, Chem. Ber. 97, 2567 (1964).

176 L.-L. Decroque, M. Perrier and J. Vialle, Bull. Soc. Chim. Fr. 2062 (1968).

177 A. Hordvik and P. Oftedal, Chem. Comm. 543 (1972).

178 A. Hordvik and L. Milje, Chem. Comm. 182 (1972).

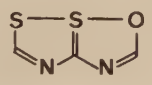
179 A. Hordvik and L. Milje, Acta Chem. Scand. 27, 510 (1973).



154

12. 1-Oxa-3,4-diaza-6,6aλ^4-dithiapentalenes.

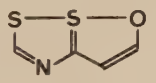
Compounds with the structure 155 have been described both by Behringer[175] and Vialle[176].



155

13. 1-Oxa-4-aza-6,6aλ^4-dithiapentalenes.

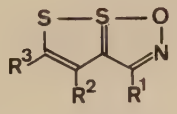
Derivatives with the structure 156 have been described by Behringer and Bender[174] who have reported UV and VIS spectra.



156

14. 1-Oxa-2-aza-6,6aλ^4-dithiapentalenes.

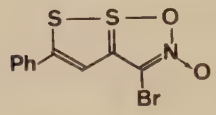
Nitrosation products of 1,6,6aλ^4-trithiapentalenes have been shown by Beer and his group to be derivatives of the ring-



157

158 R^1=PhCO, R^2=H, R^3=Ph

159 $R^1 = NO_2$, R^2=H, R^3=Ph



160

system 157[180,181] and structure determinations of 158-160 have been carried out by Paul and his group[182-185]. They have found the following S..S and S..O distances:

	158	160
S(6)-S(6a) :	2.178 Å	2.075 Å
S(6a)-O :	2.034 -	2.373 -

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180 R. J. S. Beer, D. Cartwright, R. J. Gait, R. A. W. Jonstone and S. D. Ward, Chem. Comm. 688 (1968).

181 R. J. S. Beer and R. J. Gait, Chem. Comm. 328 (1970).

182 P. L. Johnson and I. C. Paul, J. Amer. Chem. Soc. 91, 781 (1969).

183 K. I. G. Reid and I. C. Paul, Chem. Comm. 329 (1970).

184 P. L. Johnson, K. I. G. Reid and I. C. Paul, J. Chem. Soc. (B) 946 (1971).

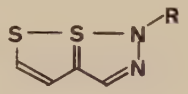
185 K. I. G. Reid and I. C. Paul, J. Chem. Soc. (B) 952 (1971).

The crystals of 159 were twins, but the results obtained proved that the nitroso group rather than the nitro group is in close contact with sulfur.

A series of compounds of this type have been prepared by Reid and his group[186]. They have reported ^{1}H NMR data on these compounds.

15. 5,6-Diaza-1,6aλ^4-dithiapentalenes.

Reid and co-workers[187] have shown that the reaction of arenediazonium tetrafluoroborate with trithiapentalenes gave

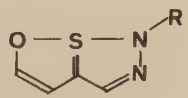


161

compounds derived from the ringsystem 161. They have reported ^{1}H NMR data.

16. 5,6-Diaza-1-oxa-6aλ^4-thiapentalenes.

A compound with the structure 162 has been prepared by Reid[187]



162

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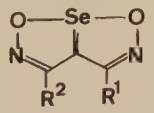
186 J. G. Dingwall, A. R. Dunn, D. H. Reid and K. O. Wade, J. Chem. Soc. (B) 1360 (1972).

187 R. M. Christie, A. S. Ingram, D. H. Reid and R. G. Webster, Chem. Comm. 92 (1973).

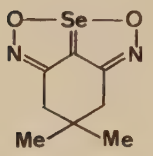
17. 1,6-Dioxa-2,5-diaza-6aλ^4-selenapentalenes.

It has been shown by Beer[188] and by Vialle[189,190] that the reaction products derived from selenium dioxide and 1,3-dioximes have the structure 163.



163

164 $R^1 = R^2 = Me$



165

Vialle gives the ^1H NMR data for this type of compounds and shows that the methyl groups of 164 are equivalent down to -60°C. X-ray data for 165 are reported[188,191]. The O..Se distances are determined to 2.017 and 2.030 Å.

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188 R. J. S. Beer, J. R. Hatton, E. C. Llaguno and I. C. Paul, Chem. Comm. 594 (1971).

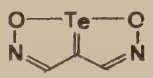
189 D. Paquer, M. Perrier and J. Vialle, Bull. Soc. Chim. Fr. 4517 (1970).

190 M. Perrier and J. Vialle, Bull. Soc. Chim. Fr. 4591 (1971).

191 E. C. Llaguno and I. C. Paul, J. C. S. Perkin II 2001 (1972).

18. 1,6-Dioxa-2,5-diaza-6aλ^4-tellurapentalenes.

The structure of the reaction product of 1,3-dioximes with tellurium dioxide has been ascribed to the structure 166[190].

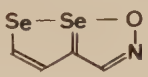


166

^{1}H NMR data indicate a symmetrical structure.

19. 1-Oxa-2-aza-6,6aλ^4-diselenapentalenes.

Compounds corresponding to the general structure 167

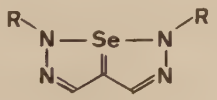


167

have been described by Reid et al[186]. They report ^{1}H NMR data for some substituted compounds.

20. 1,2,5,5-Tetraza-6aλ^4-selenapentalenes.

The structure 168 has been ascribed to the reaction



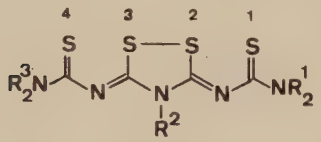
168

product from selenium dioxide and hydrazones by Vialle[190].

VII. Analogues of Extended Structures.

1. 3,5-Bis(thiocarbamoylimino)1,2,4-dithiazolidines.

Compounds of type 169 were originally described by Goerdeler and Ulmen[192] who proposed the different resonance forms 173 and 174. They have also proposed non-linear no bond resonance structures. NMR data are given for substituted

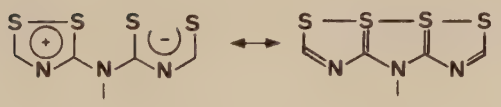


169

170 $R^1 = R^2 = R^3 = Me$

171 $R^1 = R^3 = Me$, $R^2 = Ph$

172 $R^1 = R^3 = i\text{-}Pr$, $R^2 = Me$



173 174

derivatives. Some mass spectrometrical data have been given by Oliver and Stokes[193]. Oliver and Flippen[194,195] have made X-ray structure determination on 170 and 171 and have reported the following S..S distances:

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192 J. Goerdeler and J. Ulmen, Chem. Ber. 105, 1568 (1972).

193 J. E. Oliver and J. B. Stokes, Int. J. Sulfur Chem. A2, 105 (1972).

194 J. E. Oliver, J. L. Flippen and J. Karle, Chem. Comm. 1153 (1972).

195 J. L. Flippen, J. Amer. Chem. Soc. 95, 6073 (1973).

	170	171
S(1)-S(2)	2.742 Å	2.784 Å
S(2)-S(3)	2.161 -	2.171 -
S(3)-S(4)	2.785 -	2.784 -

These distances fit nicely with structure 169 which is different from the 4-sulfur compound 109. The molecule is planar and in the case of 171 the benzene ring is twisted out of this plane by 93.8°.

Sletten[196] has determined the structure of 172 and has reported the following S..S distances:

S(1)-S(2)	2.763 Å
S(2)-S(3)	2.167 -
S(3)-S(4)	2.763 -

She suggests a bonding scheme with delocalized σ-bonding across all four sulfur atoms. A strong interaction between the outer sulfur atoms is probably caused by contribution of forms in which the terminal sulfur atoms are negatively charged. This is consistent with the results from CNDO/2 calculations, in which the terminal sulfur atoms are found to carry a negative charge of 0.44 electrons[196].

Oliver[197] has on the basis of S-alkylation of 169 suggested that no-bond resonance is operative in this system.

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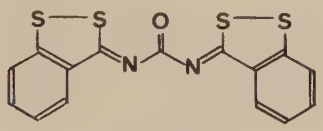
[196] J. Sletten, Acta Chem. Scand. A 28, 993 (1974).

[197] J. E. Oliver, J. Org. Chem. 39, 2235 (1974).

2. 1,3-Bis(1,2-benzodithiol-3-ylidene)ureas.

The compound 175 has been described by Klingsberg[198]

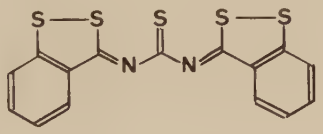


175

who gives its UV-VIS spectrum.

3. 1,3-Bis(1,2-benzodithiol-3-ylidene)2-thioureas.

Compound 176 was prepared by Klingsberg. The UV-VIS spectrum was much like the spectrum of a trithiapentalene[198].



176

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[198] E. Klingsberg, Chem. and Ind. 1813 (1968).

VIII. Concluding Remarks.

It can be concluded both from an experimental and a theoretical point of view that 1,2-dithiolylium salts as well as 1,6,6aλ^4-trithiapentalenes are true aromatic compounds.

The problem whether 1,6,6aλ^4-trithiapentalenes have real C_{2v} symmetry or time averaged C_{2v} symmetry is still not solved in a satisfactory way, but it can be said that nothing speaks against a real C_{2v} symmetry.

Concerning extended structures as well as trithiapentalene analogues, the only class which has been studied to such extent in details that it is possible to say anything definite concerning the structure is 1,2-dithiolylidene ketones. From the data available it can be estimated that 1,2-dithiolylidene ketones have to be considered monocyclic zwitterionic compounds.

Before anything can be said of the other systems we need much more theoretical and experimental material.

IX Danish Summary.

1,2-Dithiolylium salte.

Det er velkendt, at svovl kan erstatte to consecutive sp^2-hydridiserede carbonatomer i en ring. Erstatter man på denne måde 4 consecutive carbonatomer i en tropylium ion med to svovlatomer, kommer man frem til en 1,2-dithiolylium ion, som er iso-π-elektronisk med tropylium ionen.

Ligheden mellem tropylium ionen og 1,2-dithiolylium ionen fremgår af den elektrokemiske dimerisering af tropylium ionen til bitropenyl og den tilsvarende dimerisering af 3,4-disubstituerede 1,2-dithiolylium salte til dihydro tetrathiafulvalener.[13]

Det er muligt at oxidere bitropenyl til heptafulvalen, hvorimod det ikke har været muligt at lave den tilsvarende tetrathiafulvalen på denne måde.[14]

Cathodisk reduction af 3,5-disubstituerede dithiolyliumioner giver anledning til dannelse af stabile dithiolyl radicaler, som dimeriserer reversibelt ved lavere temperatur.[19] De dannede radicaler kan reduceres videre til anioner, som isomeriserer til dithioketonat anioner, som endelig kan reduceres til dianionradicaler.

Dannelse af dithiolyl radicaler og de med anionen isomere dithioketonat anioner finder deres parallel i photolysen af dithiolylium salte i ethanolisk opløsning.[25]

Det er endvidere ved massespectrometrisk undersøgelse af thermolysen af dithiolylium salte i massespectrometret vist, at de dannede nedbrydningsprodukter kan forklares på tilfredsstillende måde, hvis man antager at de primært dannede thermolyseprodukter er dithiolyl radicaler dannet ved reduction af dithiolylium ionen på anionens bekostning.[26,28]

I enkelte tilfælde, f.eks. 3-phenyl-1,2-dithiolylium salte[26] og 3-phenylthio-5-phenyl-1,2-dithiolylium salte[28] antages det, at der primært dannes en carben som dimeriserer til en tetrathiafulvalen.

Der synes således at være en snæver analogi mellem 1,2-dithiolylium saltes elektrokemiske, photolytiske og thermolytiske reaktioner.

Studier af photoelectronspectre[30] af 1,2-dithiolylium salte synes at indicere, at det er mest korrekt at opfatte dem som fuldt delocaliserede systemer i lighed med tropylium ionen. Der hersker nogen uenighed mellem forskellige forskere om den rolle, d-orbitalerne på svovl spiller i disse salte, idet man ved anvendelse af forskellige beregningsmåder og parameterisering kommer til modstridende resultater.[37,38]

1,6,6aλ^4-Trithiapentalener.

De undersøgelser, der i de sidste fem år er publiceret om trithiapentalener er centreret om to hovedproblemer.

1. I hvor høj grad trithiapentalen kan opfattes som et aromatisk 10π-electron system i lighed med naphthalen.
2. I hvor høj grad trithiapentalen besidder C_{2v} symmetri; er den symmetri som iagttages ved mange fysisk kemiske målinger reel, eller er der tale om en tidsmidlet symmetri forårsaget af, at trithiapentalenerne består af valenstautomere, der equilibrerer så hurtigt, at de overfor de hidtil anvendte målemetoder giver det samme resultat som reel C_{2v} symmetri.

Massespectrometriske undersøgelser[60,61] tyder på, at trithiapentalenerne overfor denne metode forholder sig som aromatiske forbindelser. Man får typiske "aromatiske" spectre med intense molecularioner og faldende intensitet ned gennem spectret. Denne metode, der analyserer højt anslåede tilstande, giver naturligvis ingen oplysning om symmetrien.

I forbindelse med massespectrene af trithiapentalener er det interessant at konstatere, at massespectrene af condensationsprodukter mellem 1,2-dithiol-3-thioner og aktiverede acetylener, som har været formuleret som trithiapentalen analoge bicycliske systemer, ikke udviser dette billede.[66] Disse forbindelsers massespectre er karakteriseret ved, at molecu-

larionen har relativ lav intensitet, hvorimod en ion, der svarer til en retrocycloaddition til acetylen og thion er base i spectret. Denne ions dannelse er vist ikke at være thermisk. Disse forbindelser må ifølge deres massespectre anses for at være monocycliske.

Røntgenstrukturundersøgelser[74] giver også et ret broget billede at trithiapentalenernes symmetri. Man finder ekvivalente S(1)..S(6a) og S(6a)..S(6) afstande i både symmetrisk såvel som usymmetrisk substituerede trithiapentalener, ligesom man finder uens svovlafstande i symmetrisk substituerede forbindelser. Det er således ikke muligt at komme til nogen klarhed ved hjælp af røntgenstrukturer. Dette skyldes anisotropien i krystalfasen, der bl.a. giver sig udslag i, at substituenterne er drejet ud af trithiapentalenernes plan, selv om der sterisk i det isolerede molekyle er plads til dem. Dette er f.eks. tilfældet i 2,5-diphenyl-1,6,6aλ^4-trithiapentalen.

En foreløbig meddelelse om en neutrondiffractionsmåling i gasfasen[96], hvor man ikke har disse krystaleffekter, har vist resultater som bedst tolkes, hvis man antager en symmetrisk model for den usubstituerede trithiapentalen.

ESCA og photoelectronspectroskopiske undersøgelser[68-73] har også givet modstridende oplysninger om symmetrien. Der har her været det problem, at man har måttet anvende den brede $S2p_{1/2,3/2}$ doublet, som man ikke har kunnet opløse, og man har derfor været afhængig af en matematisk deconvolution, hvor man har måttet vælge en eller anden standardbredde for svovllinien. Desuden er spectrene optaget under forskellige forhold, idet nogle er optaget af fast krystallinsk stof, andre af en tynd film på guld. Det er derfor af stor værdi, at der nu er kommet en ESCA undersøgelse på den usubstituerede forbindelse i gasfasen[69a,69b]. Denne undersøgelse er yderligere lavet på et instrument med så høj opløsningsevne, at svovldoubletten for det centrale svovlatom har kunnet opløses. Det således opnåede spectrum tyder på, at forbindelsen indenfor ESCA's tidsskala 10^{-14}-10^{-16} sekund har C_{2v} symmetri.

Den samme konklusion er man kommet til ved at studere ^{13}C NMR spectre af en række substituerede såvel som usubstitueret trithiapentalen.[114,115] Chemical shift af C(3a) tyder på, at der er tale om et bicyclisk system.[114]

Hvis man havde en hurtig tautomeri mellem to monocycliske former, skulle man vente at finde forskellige relaxationstider for C(2) og C(3). Dette viser sig ikke at være tilfældet.[114] Man må derfor konkludere, at indenfor ^{13}C NMR spectroskopiens tidsskala er der intet, der strider mod den antagelse, at trithiapentalen er et bicyclisk system, der besidder C_{2v} symmetri.

De teoretiske undersøgelser af trithiapentalener har ligeledes beskæftiget sig med forbindelsernes symmetri. Desuden har spørgsmålet om svovls d-orbitalers betydning for beskrivelsen af strukturen af disse forbindelser været genstand for talrige undersøgelser.

Det teoretiske billede af trithiapentalenerne er imidlertid ikke mere klart end det experimentelle. Forskellige forfattere kommer til forskellige resultater afhængig af den beregningsmetode, de har anvendt. Semiempiriske beregninger viser et bredt potentialminimum for den usubstituerede forbindelse, hvorimod empiriske beregninger giver en usymmetrisk struktur med et dobbelt minimum.

En ab initio beregning[72] af totalenergien for den symmetriske såvel som for den usymmetriske struktur viser, at den symmetriske har en energi, der er 4×10^{-6} au lavere end den usymmetriske. Hvis denne værdi er significant, er det letforståeligt, at systemet let deformeres af substituent- og krystaleffekter.

Det er vist, at ser man bort fra d-orbitalerne, vil en usymmetrisk struktur være favoriseret, medens en symmetrisk vil være favoriseret, hvis man medtager d-orbitalerne. Dette er i modstrid med andre forfattere, som ved beregning af energien med og uden d-orbitaler hævder, at disse kun er af ringe betydning for beskrivelsen af systemet.

Man må formentlig på det foreliggende grundlag konkludere, at i øjeblikket er hverken det experimentelle eller det teoretiske materiale tilstrækkeligt til, at man kan afgøre om trithiapentalen har et dobbelt eller et enkelt potentialminimum.

α-(1,2-Dithiol-3-yliden) ketoner og aldehyder.

Det er vist[116a,116b], at 1,2-dithiolyliden ketoner som f.eks. α-(4,5-diphenyl-[1,2-dithiol-3-yliden])acetophenon ved en elektrokemisk oxidation giver dimere dicationer, hvor dimerisationen er foregået på det sted, hvor der er hydrogen. Behandles disse dicationer med DDQ, får man nye dicationer med en dobbeltbinding mellem de to halvdele. Disse nye dicationer kan reduceres cathodisk til neutrale "dimere" dithiolyliden ketoner. At "dithiolyliden ketondelen" er intakt ses af, at de således opnåede forbindelser kan sulfureres med phosphorpentasulfid til "dimere" trithiapentalener.

Det er blevet postuleret at 1,2-dithiolyliden ketoner ved photolyse giver O-S bundne valenstautomere[117], der reversibelt går tilbage til udgangsmaterialet ved en thermisk proces. Det er senere vist, at photoprodukterne ikke har den postulerede struktur, men er de isomere trans 1,2-dithiolyliden ketoner[118,119]. I forbindelse med disse undersøgelser er det vist, at reaktionsproduktet mellem phenylacetylen og thioeddikesyre, som er postuleret at være en stabil trans trithiapentalen[58], i virkeligheden er den isomere 1,3-dithiolyliden propanthion[59]. Dette reaktionsprodukt kan desulfureres, og man havde postuleret en stabil trans 1,2-dithiolyliden keton struktur for den desulfurerede forbindelse, hvilket er i strid med de photokemiske iagttagelser. Den desulfurerede forbindelse må ligeledes antages at være et 1,3-dithiol derivat.

ESCA spectroskopiske undersøgelser[29] af dithiolyliden ketoner tyder på, at de må opfattes som monocycliske mesoioniske forbindelser med en negativ ladning på oxygen og en positiv, delocaliseret ladning på dithiolringen. Det samme resultat er man kommet til ved IR studier af forbindelser, der

er beriget med ^{18}O.[129] Det kan her vises at C=O bidraget til "carbonylabsorptionen" er så lav som 27% i visse dithiolyliden ketoner.

CNDO/2 beregninger er i overensstemmelse med disse observationer. Der hersker dog også ved beregningerne af disse forbindelser uenighed om den betydning, man skal tillægge d-orbitalerne på svovl. Det er beregnet, at cis-formen skulle være stabiliseret med ca. 20 kcal/mol, når d-orbitalerne tages i betragtning[122], hvilket svarer godt til de resultater, man kan beregne udfra kinetikken ved de photokemiske forsøg[119]. Tager man derimod ikke d-orbitalerne i betragtning er stabiliseringen kun ca. 4 kcal/mol.

Højere homologe af trithiapentalener.

Trithiapentalensystemet er et strukturelement, som kan udvides i det uendelige til at omfatte højere systemer bestående af 1,2-dithiolringe ved tilføjelse af en vinylenthio gruppe -CH=CH-S. Stofferne i de forskellige grupper, der kan dannes på denne måde, vil være neutrale, hvis de indeholder et ulige antal svovlatomer, og cationer, hvis de indeholder et lige antal. Det er indtil nu kun lykkedes at lave forbindelser med indtil 5 svovlatomer. Bortset fra røntgendata foreligger der meget få fysisk-kemiske data for disse forbindelser. Den forbindelsestype, der indeholder 5 svovlatomer på linie, synes at være et trithiapentalenlignende system med nogen delocalisering af electroner ud over hele systemet. Massespectre af forbindelserne tyder også på en aromatisk stabilitet[143].

En til dithiolyliden ketonerne analog forbindelse med 4 svovlatomer forholder sig photokemisk på samme måde som dithiolyliden ketonerne[149].

Der omtales i oversigten 8 sådanne homologe strukturer.

Trithiapentalen analoge.

De tre svovlatomer i 1,6,6aλ^4-trithiapentalen kan erstattes med O,Se,Te eller R-N, og man får da en række stoffer med formel trithiapentalenstruktur. Trithiapentalen systemet kan dog også modificeres ved, at man erstatter et carbon atom med nitrogen. Der er i denne oversigt kun medtaget forbindelser, der mindst indeholder eet svovl-, selen- eller telluratom i den oprindelige S..S..S række. Der omtales i oversigten 20 exempler på sådanne trithiapentalen analoge systemer. Der foreligger, bortset fra beskrivelse af deres synthese, kun en meget sparsom litteratur om de fleste af dem. Der er publiceret enkelte røntgen data og ^{1}H NMR data, som synes at antyde, at der i flere tilfælde er tale om systemer, der står trithiapentalen nær i fysisk-kemisk henseende.

Analoge til højere trithiapentalenhomologe.

I de udvidede strukturer kan man på samme måde som i de simple trithiapentalener udskifte såvel svovl som carbonatomer, og dermed fås en række nye forbindelser. Der er dog kun publiceret nogle ganske få exempler på forbindelser af denne type.

Konklusion.

Konklusionen af de foranstående betragtninger er, at det i dag kan siges med sikkerhed, at 1,2-dithiolylium salte og 1,6,6aλ^4-trithiapentalener må betragtes som aromatiske systemer med delocaliserede electroner. Hvorvidt trithiapentalen har reel C_{2v} symmetri, kan endnu ikke afgøres med fuld sikkerhed; men der er intet, der strider alvorligt derimod. 1,2-Dithiolyliden ketonerne kan bedst opfattes som monocycliske mesoioniske systemer. Om de andre omtalte forbindelsers struktur kan kun siges meget lidt. De få data, der foreligger, tyder dog for flere af de omtalte forbindelser på, at det drejer sig om trithiapentalen lignende forbindelser.

APPENDIX

Papers published February 1975 to April 1976

II. 1,2-Dithiolylium Salts.

199 N. Loyaza and C. Th. Pedersen, J. C. S. Chem. Comm. 496 (1975).
1,2-Dithiolylium ions form charge-transfer salts with the 4-phenyl-5-thioxo-1,2-dithiole-3-thiolate anion. The salt with 3,5-diphenyl-1,2-dithiolylium ions is shown to have semiconducting properties with ρ_{20} = 10^7-10^8 ohm·cm.

200 J.-M. Catel and Y. Mollier, C. R. Acad. Sci. Ser. C 280, 673 (1975).
1,2-Dithiolylium salts have been shown to form charge-transfer complexes with the anion of 1,1,3,3 tetracyanopropene. The influence of the polarity of the solvent on the position and the intensity of the charge-transfer band has been studied, and a linear relationship between the ionization energy and Kosowers index Z has been observed.

201 H. Behringer and E. Meinetsberger, Tetrahedron Letters (1975).
Reduction of 3-chloro-4,5-diphenyl-1,2-dithiolylium chloride with zink in acetonitrile or methylene chloride gives the tetrathiafulvalene 11, whereas reduction of 3,4-diphenyl-1,2-dithiolylium bromide results in the dihydro derivative 10.

III. 1,6,6aλ^4-Trithiapentalenes.

202 R. Gleiter, R. Gygax and D. H. Reid, Helv. Chim. Acta 58, 1591 (1975).
The He 584 Å photoelectron spectra of some 1,2-dithiol-3-ylidene ketones, 1,6,6aλ^4-trithiapentalenes, 1,6-dioxa-6aλ^4-thiapentalenes, 1,6-diaza-6aλ^4-thiapentalenes and 6-aza-1,6aλ^4-dithiapentalenes are discussed and the bands assigned, although the great difficulties in this assignment are pointed out.

203 L. K. Hansen, A. Hordvik and L. J. Sæthre in C. J. M. Stirling, ed. Organic Sulphur Chemistry, Structure, Mechanism and Synthesis, Butterworth, London 1975. p. 1.
The bonding in 1,6,6aλ^4-trithiapentalenes and analogous compounds is discussed on the basis of X-ray data and CNDO/2 calculations.

204 L. J. Sæthre and A. Hordvik, Acta Chem. Scand. A29, 136 (1975).
The following sulfur-sulfur distances have been found in 2-methyl-1,6,6aλ^4-trithiapentalene.

S(1)-S(6a) = 2.4311(16) Å
S(6a)-S(6) = 2.3076(17) Å

205 B. Birknes, A. Hordvik and L. J. Sæthre, Acta Chem. Scand. A29, 195 (1975).
2,5-Diphenyl-3,4-trimethylene-1,6,6aλ^4-trithiapentalene has been found to have unequal sulfur-sulfur distances.

S(1)-S(6a) = 2.329(1) Å
S(6a)-S(6) = 2.288(1) Å

The 2- and 5-phenyl groups are twisted 47.3 and 54.3° about the respective connecting bonds.

206 E. C. Llaguno and I. C. Paul, J. C. S. Perkin II 229 (1976).
The structure of 3-amino-2-methylthio-5-phenyl-1,6,6aλ^4--trithiapentalene has been determined by X-ray diffraction.

S(1)-S(6a) = 2.375(4) Å
S(6a)-S(6) = 2.266(4) Å

207 P. L. Johnson, E. C. Llaguno and I. C. Paul, J. C. S. Perkin II 234 (1976).
The symmetrically substituted 3,4-diphenyl-1,6,6aλ^4-trithiapentalene has been shown to have unequal S-S bond-lengths

S(1)-S(6a) = 2.236(4) Å
S(6a)-S(6) = 2.430(4) Å

The phenyl groups at C(3) and C(4) make angles of 74°50' and 70°18', respectively, with the central plane. Correspondence of the X-ray results with those obtained by ESCA is discussed.

208 E. C. Llaguno, C. T. Mabuni and I. C. Paul, J. C. S. Perkin II 239 (1976).
The structure of 5-methyl-3-[4-methyl-5-methylthiocarbonyl-2-thienyl]-2-methylthio-1,6,6aλ^4-trithiapentalene has been determined by X-ray analysis. The S-S- distances are very different.

S(1)-S(6a) = 2.546(6) Å
S(6a)-S(6) = 2.197(6) Å

209 G. Theodorakopoulos, S. C. Nyburg and I. G. Csizmadia in C. J. M. Stirling, ed. Organic Sulphur Chemistry, Structure, Mechanism and Synthesis, Butterworth, London, 1975. p. 306.
Ab initio calculations show that the trans isomer formed by rotation about the C(2)-C(3) bond in 1,6,6aλ^4-trithiapentalenes is less stable than the cis isomer by 15.7 kcal. mol^{-1}.

210 G. Calzaferri and R. Gleiter, J. C. S. Perkin II 559 (1975).
In connection with an extended Hückel study of the potential surface for the valence tautomerism of 4-thioformyl-1,2-dithiol-3-thione, the problem of C_s versus C_{2v} symmetry in 1,6,6a^4-trithiapentalenes is also discussed.

211 R. Steudel, Angew. Chem. 87, 683 (1975).
The bonding in 1,6,6aλ^4-trithiapentalenes and extended structures is discussed in connection with a general discussion of the sulfur-sulfur bond.

IV. α-(1,2-Dithiol-3-ylidene)ketones and aldehydes.

212 A. Josse, M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr. 1873 (1975).
^{1}H NMR spectra of α-(1,2-dithiol-3-ylidene)ketones have been studied in the presence of tris(dipivaloylmethanato)europium. It was shown that the induced shifts could be used for structure elucidations.

V. Extended Structures.

213 J. Sletten, Acta Chem. Scand. A29, 436 (1975).
Although symmetrically substituted, the sulfur row shows a pronounced deviation from twofold symmetry in 2,6-bis (p-methoxyphenyl-1,2-dithiol-3-ylidene)cyclohexanethione carbon disulfide solvate.

S(1)-S(2) = 2.113 Å
S(2)-S(3) = 2.626 Å
S(3)-S(4) = 2.396 Å
S(4)-S(5) = 2.271 Å

VI. Trithiapentalene Analogues.

214 D. H. Reid and R. G. Webster, J. C. S. Perkin I 775 (1975).
1,6-Dioxa-6aλ^4-trithiapentalenes and the corresponding 6a-selenaanalogues are shown by ^{1}H NMR studies to possess C_{2v} symmetry down to -90°C.

215 D. H. Reid and R. G. Webster, J. C. S. Perkin I 2098 (1975).
The protonation of 1,6-dioxa-6aλ^4-thiapentalene and 1,6-dioxa-6aλ^4-selenapentalene was studied by means of ^{1}H NMR spectroscopy. It was shown that O and C(3) protonation occurred under formation of 1,2-oxathiolium and 1,2-oxaselenolium cations.

216 K.-T. Wei, I. C. Paul, R. J. S. Beer and A. Naylor, J. C. S. Chem. Comm. 264 (1975).
The structure of 3,4-dimethylene-2,3,4,5-tetrahydro-2,5-bis-phenylimino-3,4-diaza-1,6,6aλ^4-trithiapentalene has been studied by X-ray diffraction. The crystallographically independent molecules are observed. The S-S bonds found are

S(1)-S(6a)	2.398 Å	2.419 Å
S(6a)-S(6)	2.369 Å	2.380 Å

217 M. Perrier, R. Pinel and J. Vialle, J. Heterocycl. Chem. 12, 639 (1975).
Mass spectra of a series of 2,5-diaza-1,6-dioxa-6aλ^4-thiapentalenes and their selenium and tellurium analogues have been reported. The spectra show intense molecular ion peaks and a fragmentation which is independent of the nature of the heteroatom (S, Se or Te).

218 R. M. Christie and D. H. Reid, J. C. S. Perkin I 228 (1976).
^{1}H NMR spectra of a series of 1,2-diaza-6,6aλ^4-dithiapentalenes and 1,2-diaza-6,6aλ^4-diselenapentalenes have been reported. The significance of ^{1}H NMR data and X-ray crystallographic data in relation to the structure is discussed.

. Analogues of Extended Structures.

219 J. Sletten, Acta Chem. Scand. A29, 317 (1975).
The structure of 3,5-bis(N,N-diisopropylthiocarboylimino)-4-(4-nitropheny1)-1,2,4-dithiazolidine has been determined by X-ray crystallographic methods. The four sulfur atoms are approximately colinear with the following sulfur distances

S(1)-S(2) = 2.747 Å
S(2)-S(3) = 2.194 Å
S(3)-S(4) = 2.838 Å